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HAMILTON HARBOUR STUDY 1975

august, 1977



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Ministry
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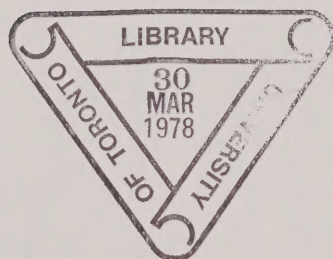
HAMILTON HARBOUR STUDY

1975

Water Resources Branch
Ontario Ministry of the Environment
135 St. Clair Ave. W.
Toronto, Ontario

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Prepared by: Lake Systems Unit
Water Modelling Section



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HAMILTON HARBOUR STUDY 1975

Table of Contents

	Page
Summary	1
Recommendations	2
Description of Harbour	3
Water Quality Studies 1975	3

Detailed Reports

Report Summary:	Dr. M.D. Palmer
Section A: Water Chemistry	Dr. D.J. Poulton
Section B: Artificial Mixing	Dr. G.D. Haffner
Section C: Sediment Chemistry	Dr. D.J. Poulton
Section D: Gas Production by the Sediments: An Oxygen Sink	Dr. W.J. Snodgrass
Section E: Biological Description of Hamilton Harbour: Bacteria and Phytoplankton	Dr. G.D. Haffner and Ms. M. Jarai



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HAMILTON HARBOUR REPORT 1975

SUMMARY

The dissolved oxygen stocks in Hamilton Harbour in 1975 were less than in 1972 even though COD loadings from the industries had been reduced by approximately 20%. Anoxic conditions still persisted in the deeper waters. An artificial mixing device (air bubbler resting on the bottom) was installed and operated from the end of June to the first week in September. Due to system breakdowns the mixing device worked sporadically at less than full capacity for most of the time. It is anticipated that the artificial mixing device should improve the dissolved oxygen levels provided operation is at capacity and commenced in May. The sediment oxygen demands are estimated at 15% of the total oxygen demand. The mean values of ammonia dropped from 1.9 to 0.85 mg l⁻¹ between 1972 and 1975 while nitrate increased indicating that nitrification was taking place during mixing. There was no trend in soluble phosphorus (filtered reactive phosphate) or total phosphorus which had monthly harbour mean values of 0.007 to 0.014 and 0.063 to 0.086 mg l⁻¹ respectively. Heavy metal concentrations in the water were below detection levels except for manganese, copper, lead, zinc and iron. Zinc levels were high enough to possibly affect phytoplankton production.

When the air diffusers were operating fully, anoxic conditions at the bottom were relieved and the chemical concentrations with depth were reasonably uniform. There was a general decline of bacterial populations and an increase in primary productivity during mixing.

In general, the sediments were severely contaminated with COD, lead, zinc, phosphorus, iron and chromium and to a lesser extent with total kjeldahl nitrogen, cadmium, nickel, manganese, mercury and copper. The concentrations exceeded IJC dredging guidelines for open water disposal. The most contaminated sediment were adjacent to the outfalls and in the deep water.

The methane and nitrogen production rates in the sediments were less than 10% of the production rates measured at the western end of the Lake Erie ($1.6 \text{ g CH}_4 \text{ m}^2 \text{ d}^{-1}$) and 50% of the methane was oxidized in the water column.

Total and fecal coliforms are generally high in surface waters near discharges. These areas exceeded the provincial guidelines and objectives for body contact recreation. The harbour had a large population of heterotrophs, and it is estimated that bacteria represent 1 mg l^{-1} of organic carbon an amount approximately equal to that in the algae of the harbour. Approximately 75% of the organic carbon came from external sources, including waste discharges.

Phytoplankton populations were dominated in the spring by diatoms and in the summer by green algae (Oocystis, Coelastrum, Kirchneriella, Ankistrodesmus, etc.). Algal densities reached a maximum greater than $10^6 \text{ } \mu\text{m}^3 \text{ ml}^{-1}$ during the summer period. Primary productivity appears to be light limited with some zinc toxicity limitations.

RECOMMENDATIONS

The aerator should be operated from mid-May to September and every effort made to reduce COD loadings further. The sources of heavy metals particularly zinc must be located and reduced. While bacterial levels have improved, further reductions in loadings are required if recreational water quality objectives are to be achieved for the northern and western portions of the harbour.

DESCRIPTION OF HARBOUR

Hamilton Harbour is an enclosed body of fresh water at the western end of Lake Ontario approximately 8 km (5 miles) in the east-west direction and 5 km (3 miles) in the north-south direction. It is connected to Lake Ontario by a ships' canal, 730m (2400 feet) long by 107m (350 feet) wide and 10m (33 feet) deep. The harbour contains approximately $2.8 \times 10^8 \text{m}^3$ ($9.9 \times 10^9 \text{ feet}^3$) of water with a mean depth of 13m (43 feet). Hamilton Harbour receives drainage from a watershed of 500 km^2 (190mi^2) through several small creeks which drain into the harbour with a total annual flow of $1.27 \times 10^8 \text{m}^3$ ($2.8 \times 10^4 \text{ MIG}$) consequently, the natural throughput is approximately 45 percent per year.

The industries located on the highly developed south shore use $26 \text{m}^3 \text{ sec}^{-1}$ (490 MIGD) of harbour water as an industrial supply, returning a similar amount of effluent to the harbour. They also depend upon the harbour for shipping of raw materials and finished products.

Municipal utilities also use the harbour as a receiving water for $10.2 \text{m}^3 \text{ sec}^{-1}$ (190 MIGD) of treated wastes and for untreated storm sewer overflows estimated at $0.1 \text{m}^3 \text{ sec}^{-1}$ (1.9 MIGD) during overflow periods. Together with the natural flow, sewage and waste effluent discharges result in a total annual flow of $4.5 \times 10^8 \text{m}^3$, or a throughput of approximately 160 percent per year. Presently, the harbour is also used for recreational boating.

WATER QUALITY STUDIES 1975

The study of Hamilton Harbour in 1975 was part of a continuing program of water quality surveillance which has been documented in reports published in 1974 and 1975, but differed as a result of these earlier studies. The purposes of the original study were to determine existing water quality and

its trends, to identify water quality problems and recommend corrective measures and to determine the effects of land filling on water quality. Interpretation of the earlier water quality data to assess the effects of abatement measures and determine the most effective abatement processes was difficult as data were not synoptic because it was not physically possible to sample the number of locations designated in a short period of time using conventional boat sampling techniques. To reduce this difficulty, survey activity was centered on four sampling locations starting in 1975. Previous studies have indicated the requirement for specific studies related to the oxygen processes; these were incorporated to improve dissolved oxygen budget computations. The 1975 study was important for the assessment of abatement processes as several industries had reduced their chemical oxygen demand (COD) loadings and an artificial mixing device was installed to improve dissolved oxygen levels in the harbour. While the mixing device operated sporadically in 1975, observations during the latter part of July when effective mixing occurred are important and are discussed in a separate section.

This report consists of five technical sections as follows:

- A. Water chemistry
- B. Mixing
- C. Sediments
- D. Methane production and oxidation
- E. Phytoplankton-Bacteria

The following portions of this introduction summarize each section. An independent report on the effects of mixing entitled "Biological Survey of Hamilton Harbour 1975" by G.P. Harris is available from the Biology Department, McMaster University, Hamilton, Ontario.

A. Water Chemistry

The dissolved oxygen stocks in 1975 were less than in 1972 even with improved treatment and artificial mixing. It is estimated that to achieve 5 mg l^{-1} dissolved oxygen in the hypolimnion $1.2 \times 10^4 \text{ kg O}_2$ is required per day. If installed in mid- or late- May, an artificial mixing device should provide at least part of this stock. Estimates of oxygen depletion rates at stations 258 and 4 in June 1975 indicate a combined sediment and water column oxygen demand of 0.06 to $0.16 \text{ g m}^{-2} \text{ hr}^{-1}$, suggesting that a higher rate of oxygen input will be required during artificial mixing for complete oxidation of the sediments.

Nitrogen component stocks in the harbour revealed similar seasonal variations in 1975 compared to 1972. Ammonia values were generally lower (compared to 1972 values), with mean values of 0.2 to 3 mg l^{-1} in 1975. Mean nitrate concentrations on the other hand were slightly higher ranging from 1.3 to 2.5 mg l^{-1} . Variations in hypolimnetic nitrate concentrations provided some indication that nitrification was occurring during the mixing period. Denitrification was evident at other times when vertical exchange was more restricted.

There was no significant trend in soluble phosphorus (ortho phosphate - filtered reactive) (mean values 0.007-0.014 mg l^{-1}) or total phosphorus (mean values 0.063-0.086 mg l^{-1}) although soluble phosphorus tended to be higher in the hypolimnion. The nitrogen/phosphorus ratio ranged from 50 to 80.

Maximum spring surface values of 1.4 mg l^{-1} silicate (1.3 mg l^{-1} at the bottom) were reduced to levels which could be limiting for phytoplankton production, e.g. 0.15 mg l^{-1} at the surface and 0.4 mg l^{-1} at the bottom by mid summer. Silicates were uniformly distributed with depth during mixing. The seasonal and depth dependence of silicate does not correlate with nitrate or phosphorus as it does in Lake Ontario.

Heavy metal concentrations in the water were generally low with manganese ($0.06-0.13 \text{ mg l}^{-1}$), copper ($0.01-0.03 \text{ mg l}^{-1}$), lead ($0.01-0.05 \text{ mg l}^{-1}$) within analytical ranges and with nickel, cobalt, chromium, cadmium and molybdenum below detection levels. In general, no spatial variations were present with the exception of manganese. Zinc levels, which reached values of 0.13 mg l^{-1} , were high enough to possibly suppress phytoplankton production. Mean surface iron concentrations of 0.3 mg l^{-1} and bottom values of 0.6 mg l^{-1} from mid-August to mid-September indicate that iron is being released from the sediments during anoxic conditions.

The mineral chemical equilibria indicated Hamilton Harbour was super-saturated in calcite and dolomite from the spring which differs from Lake Ontario where super-saturation does not occur until summer. This indicates the effect of discharges and is a function of the harbour pH, diatom production and atmospheric loading.

Conductivity in Hamilton Harbour ranged from 450 to 550 $\mu\text{mhos cm}^{-1}$ compared to Lake Ontario waters with a conductivity of 330 $\mu\text{mhos cm}^{-1}$. The range of ionic components in the samples is as follows:

	Hamilton Harbour % (based on moles)	Lake Ontario % (based on moles)
$\text{CO}_3^{=}$	1	1
HCO_3^{-}	15 - 16	21
$\text{SO}_4^{=}$	15 - 18	12
Cl^{-}	20 - 22	17
NO_3^{-}	1 - 2	-
Ca^{++}	27	33
Mg^{++}	8 - 9	7
Na^{+}	10	8
K^{+}	2	1
NH_4^{+}	1	-

The biodegradable portion of conductivity in Hamilton Harbour is 2 to 3%.

B. Artificial Mixing

Bottom air bubblers were operated from the end of June to the first week in September, to artificially mix the harbour. The mixing system consisted of four independent air diffuser lines approximately 300 m long supplied from a shore based compressor. Operational difficulties with the bottom diffusers, due to Great Lakes shipping interfering with the lines, resulted in only one, two-week period at the end of July and beginning of August when sufficient air ($0.17 \text{ m}^3 \text{ sec}^{-1}$) was being released to effectively mix the Harbour waters. This section discusses the observations during that period.

One expects that one of the immediate results of effective mixing would be surface cooling not associated with atmospheric events. Indeed during the mixing period surface waters cooled from 26 to 22°C in the vicinity of the bubbles. Before mixing, dissolved oxygen (DO) was essentially absent through most of the hypolimnion, however during mixing DO levels were greater than 1 mg l^{-1} throughout the water column. Eh profiles became orthograde during mixing. It was difficult to relate water chemical changes to mixing as the harbour is very dynamic with large spatial and temporal variations typical at many locations. There were no distinct trends in total phosphorus or soluble phosphorus although it was established that phosphorus fluctuations were not a function of algal production. Nitrification was present during mixing while denitrification occurred before and after mixing. There was a general decline of bacteria populations with the exception of sulphur oxidizers. High phytoplankton production occurred with a change in composition and abundance. In particular an isolated growth of Ankistrodesmus and Kirchneriella occurred. A peak algal volume of $8. \times 10^7 \mu\text{m}^3 \text{ ml}^{-1}$ was measured during mixing. The zooplankton biomass also peaked during the mixing period.

C. Sediment Chemistry

Sediment chemistry is important in the consideration of the harbour water quality as many of the discharged chemicals terminate in the sediments by adsorption, chemical precipitation and biological uptake. These substances can degrade the water quality by mechanical resuspension, redissolution under anoxic conditions, or recycling by biological processes. In 1975, 21 locations were sampled 3 times: once with a dredge and twice with single or multiple Phleger corers. Additional single dredge samples were obtained in Cootes Paradise and the Desjardins Canal. These samples were analyzed for aluminum, chromium, copper, nickel, zinc, lead, cadmium, manganese, iron, calcium, magnesium, mercury, cobalt, molybdenum, COD, BOD, LOI, total Kjeldahl nitrogen, total phosphorus and acid extractable phosphorus. Primarily the cores provided details on the historical contamination of the sediments. The sediments were found to be heavily polluted with COD, lead, zinc, phosphorus, iron and chromium and moderately polluted with total kjeldhal nitrogen, cadmium, nickel, manganese, mercury and copper. All metals except cobalt were considered to be excessive in concentration compared to other lake sediments. The most polluted sediments were near Randles Reef, Ottawa Street Slip, Windermere Basin and the deep water.

The mean total phosphorus and acid extractable phosphorus were 2.3 and 1.7 mg g^{-1} respectively indicating that most of the phosphorus was inorganic in form and the main source of phosphorus appeared to be the Hamilton sewage treatment plant where local sediments had a concentration of total phosphorus of 12 mg g^{-1} (high concentrations also existed in the deeper waters). From the core analysis the phosphorus loadings have been increasing over recent years. The mean total Kjeldahl nitrogen value of 3.6 mg g^{-1} is similar in magnitude to other Great Lakes sediments. As in other Great Lakes sediments, higher total Kjeldahl nitrogen was found in

muds compared to sands or silts. Total Kjeldahl nitrogen had a similar distribution to phosphorus with values of 8.5 mg g^{-1} near the Hamilton sewage treatment plant outfall.

To establish a pattern of sediment contamination it is necessary to remove the dilution of the sediment with inert materials. A method called "ratio matching" was applied in the report on the 1974 investigations; however, this method was found to be sensitive to the number of contaminants used. In this report the "ratio matching" method is refined by comparing similarity coefficients to random log-normally generated distributions and applying factor analysis to the similarity coefficients. The sediments adjacent to the entrance to Cootes Paradise, Windermere Basin, Randles Reef and off the Ottawa street slip were identified as uniquely contaminated regions. Sediment contamination of the central and southeastern portion of the harbour were related directly to the industrial discharges and the Hamilton sewage treatment plant; common physical and chemical transport processes resulted in similar distributions of different pollutants throughout this area. Mass exchange through the Burlington ship canal was effective in maintaining higher quality sediments near the harbour entrance and the northeast portion of the harbour.

D. Methane Production

Methane production results from a conversion of carbohydrates, fats and proteins to acids and alcohols which are then converted to methane or carbon dioxide. Methane rises into the water column and is oxidized to carbon dioxide. Methane gas was collected at the bottom and top of the water column at two locations. The mean methane production at the bottom was 87 and $157 \text{ mg m}^{-2} \text{ day}^{-1}$ at the western and eastern end of the Harbour respectively. A typical value for the western end of Lake Erie is $1.6 \text{ g m}^{-2} \text{ day}^{-1}$. Mean methane transport rates at the surface were 38 and $76 \text{ mg m}^{-2} \text{ day}^{-1}$ at the

western and eastern end of the harbour respectively. Consequently approximately 50% of the methane is oxidized in the water column. The mean production of nitrogen at the bottom was 68 and 89 mg m⁻² day⁻¹ and at the surface the rate of collection was 57 and 83 mg m⁻² day⁻¹ at the western and eastern end of the harbour respectively. Methane and nitrogen were the only gases collected and there appeared to be no seasonal trend in the gas production. It is estimated that the sediment oxygen demand and methane oxidation had a total oxygen demand of approximately 2g O₂m⁻² day⁻¹.

E. Bacteria and Phytoplankton

Chlorophyll a is not considered an appropriate technique for measuring biomass in Hamilton Harbour where bacteria populations are large. (The chlorophyll a content/unit algal volume varied from 2.4×10^{-10} to 1.0×10^{-8} µgµm⁻³). While the maximum chlorophyll a has changed erratically since 1972 biomass has remained relatively constant.

Carbon cycles, production of CO₂ or methane, sulphur and nitrogen cycles are functions of bacterial populations. For 8 taxa, bacterial crops were of the order of 10⁵µm³ml⁻¹. Abundance of pseudomonas and enterococci was generally low in open waters. Fecal coliform, total coliform and nitrosomonas were frequently high in surface waters near municipal outfalls. Except at the western end of the harbour, total coliform levels exceeded 1000 per 100 ml and were above the I.J.C. objective for contact recreation. Fecal coliforms were below the objective of 200 per 100 ml except in the vicinity of the Hamilton sewage treatment plant outfall. The harbour had a large resident population of heterotrophs which were important in stabilizing the large organic loadings to the harbour. There is no indication that heterotrophs were nutrient limited. It is estimated that bacteria represent 1 mg l⁻¹ of carbon while phytoplankton represent another mg l⁻¹ of carbon. As the total organic carbon was 7 to 8 mg l⁻¹, allochthonous material accounted for 75% of the organic

carbon in the harbour waters. No trends of nitrosomonas, sulphur reducers and oxidizers were observed.

In general green algae dominated the phytoplankton in the late spring and summer with diatom populations dominating in the early spring. Genera such as Oocystis, Coelastrum, Lagerheimia, Selenestrum, Kirchneriella and Ankistrodesmus were abundant in late spring with Chlamydomonas and Pandorina morum (Muell) Borg being frequently observed. The most important species in the summer were Oocystis Borgei Snow, Pandorina morum and Cryptomonas spp. There was no indication of nutrient limitation, and phytoplankton production appears to be light limited with some evidence of zinc toxicity. The lack of blue-greens is attributed to the physically unstable water column. More than 80% of the phytoplankton carbon was produced in the top two meters.

HAMILTON HARBOUR STUDY '75

section A

Water chemistry

SUMMARY

WATER CHEMISTRY

WATER CHEMISTRY WAS SAMPLED AT FOUR LOCATIONS IN THE HARBOUR APPROXIMATELY WEEKLY DURING 1975 IN ORDER TO ASSESS THE EFFECTIVENESS OF ARTIFICIAL MIXING AND ITS EFFECTS ON WATER CHEMISTRY, INCLUDING NUTRIENT CONCENTRATIONS AND DISSOLVED OXYGEN STOCK.

ARTIFICIAL MIXING ALLOWED AN INCREASE OF BOTTOM DISSOLVED OXYGEN CONCENTRATIONS TO AROUND 2 MG/L COMPARED WITH NEAR ZERO VALUES BEFORE AND AFTER MIXING. HOWEVER, THE MID-SUMMER DISSOLVED OXYGEN STOCK IN 1975 WAS ONLY ABOUT 1.0×10^6 KG, COMPARED TO ABOUT 1.3×10^6 KG IN 1972. IN ORDER TO MAINTAIN THE HYPOLIMNETIC DISSOLVED OXYGEN CONCENTRATION AT 5.0 MG/L, THE DISSOLVED OXYGEN STOCK WOULD BE 1.6×10^6 KG. TO MAINTAIN THIS VALUE, IT IS ESTIMATED THAT THE MIXING WOULD HAVE TO SUPPLY AT LEAST 1.2×10^4 KG/DAY OXYGEN.

AMMONIA AND TOTAL KJELDAHL NITROGEN VALUES ARE LOWER IN 1975 THAN 1972, WHILE NITRATE VALUES ARE SLIGHTLY HIGHER. HYPOLIMNETIC NITROGEN CONCENTRATIONS ARE CONTROLLED BY REACTIONS AT THE SEDIMENT-WATER INTERFACE, WITH NITRIFICATION AND AMMONIA UPTAKE UNDER OXIC CONDITIONS, INCLUDING ARTIFICIAL MIXING, AND DENITRIFICATION AND SOME AMMONIA RELEASE OCCURRING UNDER ANOXIC CONDITIONS.

PHOSPHORUS VALUES WERE SIMILAR TO THOSE OBSERVED IN 1972, WITH NO SIGNIFICANT SEASONAL TRENDS OR RELEASE FROM ANOXIC SEDIMENT BEING OBSERVED.

THE SILICA CONCENTRATIONS SHOWED A SPRING DECREASE, LIKELY RELATED TO DIATOM GROWTH. DURING STRATIFICATION, EPILIMNETIC SILICA CONCENTRATIONS ARE GREATER THAN HYPOLIMNETIC CONCENTRATIONS; NEARLY UNIFORM DEPTH PROFILES WERE OBTAINED DURING ARTIFICIAL MIXING.

ALTHOUGH NO RELEASE OF DISSOLVED IRON FROM THE SEDIMENTS WAS OBSERVED BEFORE THE MIXING PERIOD, SOME RELEASE DID OCCUR UNDER HYPOLIMNETIC ANOXIA IN SEPTEMBER 1975.

CONTRIBUTIONS OF VARIOUS IONS TO THE CONDUCTIVITY OF HAMILTON HARBOUR WATER INDICATED THAT NON-CONSERVATIVE (BIO-DEGRADABLE) MATERIALS CONTRIBUTE 2 TO 5% TO THE OBSERVED CONDUCTIVITY, AND THAT CHLORIDE AND SULFATE CONTRIBUTE AN AVERAGE OF 36% TO THE CONDUCTIVITY, COMPARED TO 29% FOR LAKE ONTARIO AND 22% FOR MEAN RIVER WATER.

1975 HAMILTON HARBOUR WATER CHEMISTRY

A chemical survey of the water was carried out during 1975. The harbour was sampled approximately weekly from late April to mid-August, and at irregular intervals of one to three weeks thereafter. Most chemical parameters were measured at four sampling stations (Figure 1). In addition, monthly surveys were carried out for nutrients (eight sampling stations) and dissolved oxygen (18 stations). The purposes of the chemical survey were to determine water quality trends in Hamilton Harbour, to assess the dissolved oxygen depletion and measure the effects of abatement procedures in operation.

Details on the environmental controls and their effects on the harbour chemistry and biology have been presented in Section B; in this section the chemical results are discussed in detail with reference to the artificial mixing and loading reductions where appropriate. This section has been broken down into several portions to facilitate the discussion of the various aspects of the harbour chemistry. As redox potential is fundamental to most of the discussions, a brief mention of the measurements and their limitations is given first. This is followed by subsections on dissolved oxygen, nitrogen, phosphorus, silica, heavy metals and minerals.

REDOX POTENTIAL MEASUREMENTS

Redox potentials were measured in Hamilton Harbour by the NERA water quality monitor at stations 4, 258, and 270 on various dates between June and September, 1975. Depth profiles (Figure 2) of redox frequently presented an orthograde distribution, with the value constant with depth at 100 to 200 mv. At other times, clinograde distributions were found with the potential approaching zero at depths greater than about 12 m.

Surface redox potentials of 100 to 200 mv are lower than those normally observed. Water saturated with dissolved oxygen has a redox potential E_H of 800 mv or $pE=13.6$ at pH 7 and $25^\circ C$ (Stumm and Morgan, 1970, p. 328). pE is a conceptual term which can be regarded as the negative logarithm of relative electron activity, and is defined by

$$pE = \left(\frac{F}{2:303 RT} \right) E_H = \frac{E_H}{0.059} \quad \text{at } 25^\circ C$$

where:

F is the Faraday constant

R is the gas constant

T is absolute temperature ($^\circ K$)

However, this value is never observed when measuring E_H with a platinum electrode in natural waters. Under oxidizing conditions, traces of oxygen are dissolved in the electrode, which then behaves as a $Pt-O$ electrode, generating a potential E dependent upon pH according to the equation (Whittfield, 1974).

$$E = E^\circ_{Pt/Pt-O} - 0.06 \text{ pH}, \text{ where } E^\circ_{Pt/Pt-O} = 0.88 \text{ V}$$

$$\text{or } E = 460 \text{ mv at } pH = 7$$

The behavior of the platinum electrode in oxidizing systems has also been described in terms of the $PtO_2 \cdot 2H_2O$ electrode ($E^\circ=0.96$ V or $E = 540$ mv at $pH = 7$), or the so-called "irreversible" oxygen electrode (Merkle, 1955, quoted in Whittfield, 1974) ($E^\circ=0.70$ V or $E = 280$ mv at $pH = 7$). These figures represent rough upper limits to electrode potentials normally observed in aquatic systems containing dissolved oxygen; most observed data are contained by these extremes (Whittfield, 1974; Hutchinson, 1957, p. 693-694).

Therefore, some explanation of the low values of redox potentials observed in Hamilton Harbour is required. If the

redox probe has been exposed to sulfide, e.g. by contact with reducing sediments, a film of platinum sulfide may be formed. This results in decreased, drifting redox potential measurements in natural water systems (Hayes, Reid and Cameron, 1958). Such a film is not easily removed; Hayes and co-workers indicated that several rinsings in concentrated chromic-sulfuric acid were required. Despite the film, such an electrode will still respond properly to the concentrated ferrous-ferric solution used for calibration; this solution has a high redox capacity (ability to resist changes in E_H due to presence of extraneous oxidants or reductants, analogous to buffer capacity or alkalinity in pH considerations (Stumm and Morgan, 1970)). On the other hand, natural water has a low redox capacity and the effects of exposure to sulfide can be seen.

Other than that, the cause of low redox potentials must be that a redox couple other than O_2-OH^- is controlling the redox potential of the system. As nitrogen redox systems have pE^0 values in the range 4.5-6 at pH 8, this system is not likely controlling redox potential in Hamilton Harbour (observed $pE=1.7$ to 3.4).

A redox couple which may control observed E_H values is the iron system. Sillen (in Stumm and Morgan, 1970, p. 338-339) has proposed a redox titration model of seawater in which the equilibrium between $FeOOH(S)$ and $Fe_3O_4(S)$ produces a buffering system at $pE=3.7$, which has a much larger capacity than that of the oxygen system. Although this system is thermodynamically unstable with respect to oxygen, the oxidation rate of magnetite (Fe_3O_4) at room temperature is negligible. Therefore, in Hamilton Harbour, if small amounts of these oxides are present in suspended form as a result of industrial discharges, a metastable redox equilibrium may occur with a potential similar to that observed.

However, redox conditions in the iron system are influenced considerably by organic matter (Theis and Singer 1973, 1974). Tannic acid concentrations of 5×10^{-5} M, which corresponds to a total organic carbon concentration of 8.4 mg/l, will stabilize 2 mg/l ferrous iron in solution as a complex. Gallic acid and pyrogallol similarly inhibit the oxidation of ferrous ion; indeed, iron-organic complexes can participate in a catalyzed oxidation scheme in which a slow oxidation of $Fe(II)$ -organic complexes to the corresponding $Fe(III)$ complex is followed by the oxidative decomposition of the unstable $Fe(III)$ complex to ferrous iron and oxidized organic material (Theis and Singer, 1974). Similar reduction of $Fe(III)$ in a humic acid complex has also been demonstrated (Oldham and Gloyna, 1969). As the organic carbon concentration above is comparable to Hamilton Harbour values of 5 to 12 mg/l, these mechanisms could be operating. Since the redox potential of these reactions has not been measured, there is a possibility that such reactions could be influencing Hamilton Harbour redox potentials throughout the water column.

At any rate, the point at which redox potential plays its most important role is at the sediment-water interface. As discussed in sections on metals, nitrogen and phosphorus, the sediment can release substances such as ferrous iron, manganese, ammonia and soluble phosphorus under anaerobic conditions at E_H values below about 0.2 V. In order to do reliable studies of the redox regime at the Hamilton Harbour water-sediment interface, it is suggested that sediment-water systems be studied in the laboratory with an array of electrodes similar to that used by Mortimer (1941, 1971).

DISSOLVED OXYGEN

The original study (MOE, 1974) identified dissolved oxygen depletion as one of the 'most pressing' problems in Hamilton Harbour. It was recommended that chemical oxygen demand loadings be reduced by approximately 60 percent and that artificial mixing be undertaken in order to increase hypolimnetic dissolved oxygen concentrations to the criterion for fish, aquatic life and wildlife of 5 mg/l. In addition, the observed dissolved oxygen depletion curve was analyzed in terms of sediment oxygen demand results measured elsewhere by in situ and laboratory methods (MOE, 1975). Using estimated uptake rates of 0.04-0.07 g/m²-hr, an oxygen uptake of 3×10^6 kg was calculated for a 109 day period. This was twice the observed deficit of 1.5×10^6 kg (computed from observed and saturation stocks). A major reason for this discrepancy was believed to be mass exchange through the Burlington ship canal, which was estimated to supply between 4×10^5 and 4×10^6 kg of DO to the harbour. As surface DO values were generally close to (and sometimes greater than) 100% saturation, surface reaeration is not expected to play a significant role in accounting for this discrepancy despite the relatively large surface area of the harbour.

To indicate the effect of the artificial mixing program on harbour dissolved oxygen levels, dissolved oxygen-depth profiles were taken weekly at the four major sampling points (Figure 1) and monthly at eight (May and June) or eighteen (July-September) station detailed grids for DO stock computation purposes during 1975. A proposed 18-station survey in October was abandoned after the monitor failed and weekly data taken the previous day indicated complete mixing (overturn) of the harbour. In addition, digital recording current meters were operated at four depths in the ship canal for a two-month period in an attempt to improve the estimate of DO mass exchange with Lake Ontario. However, failure of two of these meters prevented such an estimate.

Dissolved oxygen stocks were computed from the 8- and 18-station surveys by methods similar to those used with the 1972 data. Briefly, the harbour was divided into regions corresponding to the sampling stations by drawing the right

bisectors of the lines joining adjacent stations, and the area, volume and average depth of each sub-region was calculated. A mean dissolved oxygen stock per unit area was calculated for each sub-region by integrating the DO-depth profile from the surface to the average sounding for each station. These values were multiplied by the area of each sub-region and summed over the entire harbour. This method (method a) was found to be somewhat unsatisfactory as it failed to take into account the variations of depth across each sub-region; i.e. the sub-regions were assumed to have vertical walls and flat bottoms. This resulted in replacing the portion of each sub-region at depths greater than the mean depth for each region with a hypothetical zone closer to the water surface, thus overestimating DO stock since the deep zone was usually depleted in DO.

The method was modified by further dividing each region into six (or fewer, depending on water depth) vertical zones at depths corresponding to the marine chart contours which had been used in volume computations. This was called method (b). Dissolved oxygen stocks were then calculated for each zone from the average concentrations measured within that zone and its volume and summed over the harbour. If there was no concentration available for any zone (representing a depth greater than that available at the sampling location), the DO concentration was estimated from the surface DO and the harbour-wide average DO (depth)/DO (surface) ratios for that date. As well, a DO stock value was estimated from DO-depth profiles obtained from surface DO and average DO (depth)/DO (surface) values throughout (method c). This method, as used with the 1972 data, averages the effect of internal waves and periodic lake motions on the harbour water (MOE, 1974) over the entire bay.

Results of DO stock calculations by these methods are given in Table 1. Included also is an estimation of what the DO stock would be if the entire hypolimnion were aerated to the 5 mg/l criterion value. This was obtained by computing DO stocks for each sub-region divided into depth zones as stated above, except that 5 mg/l was used for a DO value in all zones in which the DO was less than this result. Methods (b) and (c) give results within less than 3 percent of each other, a discrepancy which is less than the experimental errors involved in DO measurement and volume estimation. The results of method (a) average about 5 percent higher than those of methods (b) and (c), for the reason stated above.

The DO stock calculated by these methods is compared with the 1972 result in Figure 3. It is evident that a much more serious DO depletion problem occurred in 1975, despite

operation of the aerator and the improved treatment facilities of the steel companies. The July figure indicates that the depletion had developed before commencement of diffuser operation. This may indicate an increased sediment oxygen demand problem, but it is probable that at least a portion of the added deficit resulted from the warm, relatively calm weather in May and June 1975, which allowed a rapid development of stratification. Average air temperatures in May and June 1975 at Hamilton Airport were 16.1°C and 18.9°C respectively, compared with 1972 figures of 14.1°C and 16.3°C, and long-term normal values of 12.6°C and 18.1°C. May and June 1975 average wind speeds were 4.0 and 4.5 m/sec, respectively, slightly lower than 1972 values of 4.4 and 4.7 m/sec. This supposition is supported by preliminary results of in situ sediment oxygen demand measurements, which indicate demands of approximately 0.05 g/m²-hr, or about the same as estimated from a previous survey of sediment oxygen demand measurements (MOE, 1975).

Table 1 indicates that the deficit in July from the stock representing a minimum hypolimnetic DO of 5 mg/l is about 0.5×10^6 kg. As the corresponding deficit for early June is very small, it is evident that artificial mixing, combined with natural reaeration of low DO water brought to the surface, would have to supply at least 1.2×10^4 kg oxygen per day to maintain hypolimnetic DO at 5 mg/l. Various equations have been proposed to estimate the rate constant for reaeration, mainly in rivers and estuaries (Wilson and McLeod, 1974; Owens, 1973). However, as Wilson and McLeod (1974) state that none of the equations describe the reaeration process adequately, only an order of magnitude estimation for the exchange coefficient f may be given, using the proposed equation of Owens (1973):

$$f(20^{\circ}\text{C}) = 22.2U^{0.67}H^{-0.85}$$

Assuming an average velocity U of 3 cm/s and depth H of 13 m, the estimated exchange coefficient f is 0.2 cm/h, or an absorption of 0.05 gO₂/m²-d for each mg/l deficit. For a surface deficit of 1 mg/l, about 1×10^3 kg oxygen per day would be supplied by reaeration, i.e. most of the additional oxygen would have to come from artificial mixing, or lower DO water would have to be moved to the surface during mixing to satisfy the deficit. Considering an increased rate of sediment oxygen uptake at high DO concentration, the actual required rate will be somewhat higher.

Weekly data are presented in isopleth form in Figure 4. Figure 5 presents some dissolved oxygen-depth profiles observed at stations 4, 258 and 270 during the mixing period. The effect of artificial mixing, which is not

noticeable in the monthly stock calculations is seen clearly in Figure 4 as a depression in the depth of the isopleths at July 16, followed by an increase in the bottom dissolved oxygen concentration at stations 258 and 4 between July 16 and 23. Slightly elevated wind speeds between July 10 and 16 (4.1 m/sec compared to July average 3.7 m/sec) may have increased surface DO at this time. Although the isopleths were depressed slightly again in early August, the result in this case varies from one station to another, and may be caused by internal wave motions. These changes do not correlate with any natural aeration, as the average wind speed for August 1-6 was only 3.0 m/sec, compared to the August mean of 3.9 m/sec.

The most significant time of bottom DO depletion is clearly visible during June, a feature which was not detected during 1972 due to the lack of spring sampling. For the period of greatest rate of bottom DO depletion, the rate of sediment oxygen demand was estimated from vertical integration of the hypolimnion portion of the DO-depth curves. Results for two time periods, June 4-11 and June 11-25 are given in Table 2. The considerably lower rate at station 270 undoubtedly derives from the shallow water depth (thin hypolimnion) at this station, combined with horizontal mixing processes, which will evenly distribute the low-DO water throughout the hypolimnion. In addition these estimates of hypolimnetic DO depletion are subject to an error derived from the action of internal waves on the thermocline position (i.e. the non-synoptic nature of the data sets). A comparison with results obtained by G. Harris (1976) is also given in Table 2. This was obtained from his data at mid- and bottom depths, and was recalculated to our units assuming an average hypolimnetic depth of 10 m. The result is in agreement with our data.

Although this method only provides a rough estimate of the rate of DO depletion, it is interesting to note that the rate for the period June 4-June 11 is comparable to the estimates used in discussing the 1972 data (MOE, 1975), but the rate for June 11-25 is more than twice as great. It should be noted that these figures include the water DO demand due to phytoplankton decay and waste discharges, estimated at 1/3 of the total DO demand (MOE, 1975). Despite this fact, it is evident that the rate of sediment oxygen depletion may be more severe than presently suspected, and that a more rapid rate of oxygen input will be required during artificial mixing for complete oxidation of the sediments.

In 1975, preliminary estimates of oxygen demand in the water column due to methane oxidation were obtained by W. Snodgrass. Oxidation rates were determined as the difference in the amounts of methane collected between the surface and bottom

of the water column. Results were converted to oxygen demand assuming complete oxidation according to the reaction $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$. Results at stations 4 and 270 indicate oxygen demands of 0.015 and 0.009 g/m²-hr, or 15 to 35% of the approximate sediment oxygen demand. These are equivalent to a volume demand of 0.76 mg/m³-hr, assuming oxidation occurs throughout the water column. Over a four month period of summer stratification, this is equivalent to a hypolimnetic depletion of 2.2 mg/l. If the hypolimnion is considered to include the portion of the harbour below a depth of 6.6 m or a volume of $146 \times 10^6 \text{ m}^3$, this will produce a DO stock depletion of $0.32 \times 10^6 \text{ kg}$ in four months. Thus, the methane oxidation process is a small but significant portion of the total oxygen demand in Hamilton Harbour.

Plans for 1976 include another attempt at measuring DO mass exchange through the ship canal with an array of four current meters. In addition, the sediment oxygen demand is to be measured in situ on a weekly basis at locations representative of various sediment characteristics, and additional measurements of methane production and oxidation will be done.

NITROGEN

Data for 1975 are compared with results of previous years using techniques similar to those used in the first Hamilton Harbour report. In tables 3 and 4, June to October averages for each station, and harbour-wide averages for each month are compared for 1966 to 1975. Ammonia values in 1975 are generally higher than those observed in the small data set collected in 1974, but still lower than 1972 levels. However, due to fluctuations observed in both years (the standard deviation of the July 1974 figure was 175 percent of the mean; in addition, ammonia values over most the harbour were less than 0.01 mg/l on August 6, 1975), no significant between year variation in ammonia can be considered to exist in 1974-75. At any rate, it is better to compare 1975 with 1972 due to the small amount of 1974 data available. Such a comparison is made on a seasonal basis in Figure 6 for ammonia, and Figure 7 for total Kjeldahl nitrogen. Figure 8 gives the depth-time distribution of 1975 ammonia data. The seasonal trend, a decrease from spring maximum to fall minimum, is similar in 1972 and 1975. This is thought to result from biological uptake and nitrification of ammonia having accumulated from industrial loadings in the winter. Organic nitrogen (total kjeldahl N minus ammonia) is similar in both years at about 1 to 1.5 mg/l with no seasonal trend. An exception is the very high results obtained on July 23. This coincided with maximum chlorophyll a values of up to 93 ug/l presumably related to artificial mixing. This increased organic nitrogen content may be partly a result of increased biomass, as measured by chlorophyll a; surface organic

nitrogen concentrations at stations 4, 252, 258 and 270 were 4.0, 3.7, 2.6 and 2.9 mg/l N respectively, while chlorophyll a values were 57, 93, 27 and 16 ug/l. Both parameters were stratified with higher values in the epilimnion. However, a cause-effect relationship cannot be definitely proven.

As with ammonia, it is best to compare 1975 nitrate data with 1972, rather than 1974. This comparison is shown in Figure 9; depth-time distributions of nitrate and nitrite are given in Figures 10 and 11, respectively. Nitrate data in 1975 showed a similar seasonal trend to 1972 with average values about 0.5 mg/l higher in 1975. Maximum surface values were recorded on June 4 and August 13, coinciding with relatively lower ammonia readings. The former date is also the date of a very strong nitrite maximum, most pronounced at station 4 (1.6 mg/l NO₂-N in the epilimnion and 1.2 mg/l NO₂-N in the hypolimnion). In addition, on June 4, the epilimnion of station 4 was characterized by slightly decreased pH, very low (<1 ug/l) dissolved phosphorus and relatively low chlorophyll a. The epilimnion at other sampling stations shows these effects to a lesser extent. Compared to other sampling dates, June 4 represents a unique chemical environment. It is possible that the redox potential achieved a value which favored nitrite; the presence of a high bacteria count on this date is significant, and this may have led to optimum conditions of nitrification.

Seasonal variations of nitrite are interesting. As mentioned above, this parameter was found in a concentration of 1.6 mg/l in the epilimnion of station 4 on June 4. High values were found throughout the harbour at all depths on this date, the mean value being 1.1 mg/l NO₂-N. By contrast, on July 16 and August 6, most of the harbour contained less than 0.1 mg/l NO₂-N. Values observed in 1972 for this parameter were generally about 0.2 mg/l in the epilimnion from late July to early October, being slightly less at the end of August. Maximum nitrite values of 0.5 to 0.7 mg/l NO₂-N for 1972 were seen in late October; however, no samples were obtained in June of that year.

The significance of the seasonal variations in nitrite is not clear. They may be related to the variation in the relative concentrations of nitrogen species with redox potential; over a small range the dominant species changes from ammonia to nitrite to nitrate (Stumm and Morgan, 1970).

Nitrate was strongly depth stratified in both 1972 and 1975, with highest values in the epilimnion. On the other hand, the depth distribution of nitrate in 1975 was variable. During June and early July, hypolimnetic concentrations of nitrate were generally greater than epilimnetic; for most of

July, August and September the reverse was true. Denitrification of the bottom waters during the period July to September is further corroborated by an increase in nitrate during the effectiveness mixing period.

These complex depth-time variations of nitrogen species are believed to be regulated by reactions at the sediment-water interface. Evidence for this is presented below. Such reactions are complicated, involving a variety of mechanisms such as adsorption and desorption processes, mineral-water equilibria, redox reactions, and the activities of organisms such as plankton, benthic fauna and bacteria (Mortimer, 1971). Additionally, despite the decreased extent of municipal and industrial loadings, these still play a dominant role in Hamilton Harbour, as the seasonal and depth variations in nitrogen parameters have remained essentially the same, retaining at least in part several departures from the situations frequently seen in lakes, including eutrophic ones.

An important example is the depth distribution of ammonia, which frequently accumulates in the hypolimnion during summer stratification. Some evidence of this occurring in 1975 at stations 4 and 258 in the absence of artificial mixing exists; in 1972 this phenomenon was not observed. Concentrations of up to several mg/l have been observed previous to fall overturn in the English lakes (Mortimer, 1941) and in other cases (Hutchinson, 1957). This release is related to the disappearance of the oxidized microzone, as ammonia does not begin to accumulate until the sediment surface is reducing in nature. Additionally, it has been shown in laboratory experiments with Lake Mendota sediment (Austin and Lee, 1973) that ammonia is released under anaerobic conditions but adsorbed under aerobic conditions. Such results were also observed by Mortimer (1941) in his classic experiments with the aerated and anaerobic tank systems. During 1972, ammonia release was not observed in Hamilton Harbour for two reasons: (a) the presence of industrial discharges of magnitude sufficient to obliterate the effect of ammonia release; and (b) the sediment may not have achieved a sufficiently reducing condition. During 1975, artificial mixing may have suppressed ammonia release. Prior to the start of aerator operation, between July 3 and 9, ammonia release at the bottom occurred, with average bottom concentration increasing from 0.45 mg/l to 1.5 mg/l. Thereafter, ammonia concentration decreased gradually to below 0.05 mg/l on August 6-19. Following cessation of aerator operation, bottom ammonia increased to 0.4 mg/l (September). However, except for station 258 between mid-June and mid-July (before operation of more than one aerator) there was no increase in ammonia concentrations with increasing depth in Hamilton Harbour, as observed in many lakes (Hutchinson, 1957).

Another exception to usual seasonal patterns is the increase in nitrate concentration to a summer maximum. In most cases, nitrate is at a maximum in the spring; concentrations decline in the summer to near zero in the bottom waters due to denitrification and also in the surface waters due to immobilization or biological utilization (Keeney, 1973). On the other hand, sediments can be a significant source of nitrate-N. Under anaerobic conditions, nitrogen was not released from Lake Mendota sediments in the laboratory (Austin and Lee, 1973); however, the amount of nitrogen (as nitrate) released under aerobic conditions was higher by a 2-to-6-fold factor than that released (as ammonia and organic N) from the same sediments under anaerobic conditions. In early June, prior to establishment of anoxia, bottom nitrate concentrations increased from 1 mg/l to over 3 mg/l, and an inverse clinograde depth distribution, which persisted until early July, was set up. Simultaneous to this nitrate increase, a decrease in ammonia and increase in nitrite occurred. Apparently, bacterial nitrification was taking place, most vigorously at the sediment-water interface. Such nitrification has been observed to occur vigorously in well-stirred lake sediments (Keeney, 1973).

Under anoxic conditions in the hypolimnion, nitrate concentrations dropped from 3-3.5 mg/l on June 25 to 0.6-0.9 mg/l on July 16, with a clinograde depth distribution having developed, in contrast to the inverse clinograde distribution seen in June before bottom anoxia developed. This is evidence of nitrogen mineralization and denitrification. Nitrogen mineralization appears to be greater under anoxic conditions than under aerated conditions as a result of greater efficiency of conversion of organic C to cell C by heterotrophic anaerobes (Keeney, 1973). Additionally, denitrification occurs in any anaerobic microbial environment. Disagreement exists as to whether simultaneous reduction (to NH_3) and denitrification can occur, although experiments by Goering and Dugdale (1966) favored denitrification over NH_3 production. Subsequent to the commencement of artificial mixing, some nitrate release from deep water sediments occurred, with bottom water nitrate readings reaching the range of 1.2-1.5 mg/l on August 13. The increase occurred at a time when bottom dissolved oxygen readings were between 1 and 4 mg/l with a lag of perhaps one week relative to DO data. After cessation of artificial mixing, denitrification (or nitrogen reduction) took place, with the nitrate concentration dropping to 0.8-0.9 mg/l on September 9-15. Natural mixing resulted in an increase to October values of 1.5 mg/l. It is obvious that nitrate release has occurred during times of mixing, either artificial or natural. A lag of a few days or a week may be present; this is in qualitative agreement with a one-to three-day lag observed on laboratory incubation of stirred Lake Mendota sediments (Keeney, 1973; Austin and Lee, 1973).

In contrast to our conclusions, Harris (1976) found that hypolimnetic nitrate decreased during mixing. This conclusion was apparently based on one series (July 28) of low nitrate results (0.47 mg/l ($\text{NO}_3 + \text{NO}_2$)-N, compared with our value of 0.90 mg/l NO_3 -N + 0.08 mg/l NO_2 -N on July 31). The reason for this difference may have been short-term fluctuations (our results indicate a decrease in average bottom nitrate between July 23 and 31), changes after sampling or analytical errors.

The above discussion indicates that nitrogen concentration in the water is greatly influenced by sediment-water interactions. Relative release rates under anaerobic and aerobic conditions (Austin and Lee, 1973) seem to indicate that if the sediment-water interface of Hamilton Harbour is maintained aerobic during artificial mixing, increased release of nitrate will occur, leading to increased concentrations in the water column. The effect will be greater if such mixing disturbs the sediments.

On the other hand, Keeney, Schmidt and Wilkenson (1975), who performed cyclic aeration studies on experimental sediment-water systems, found that a nitrification-denitrification cycle was capable of removing one-third of the available nitrogen. This suggests that intermittent artificial mixing could lead to decreased inorganic N concentrations. However, as total inorganic nitrogen has a tendency to decrease seasonally in Hamilton Harbour (compare Figures 6 and 9), it is not possible to state whether this mechanism is operating in Hamilton Harbour. The fact that nitrogen is a component in the gas evolved from the sediments (Section D, methane production and oxidation) is evidence for denitrification in Hamilton Harbour and possible operation of this mechanism.

In Table 5, nutrient and chlorophyll stocks for 1975 are presented. These were computed by integrating average concentrations within six depth zones at each station (8-station grid) across the harbour (method (c) as used with DO). Comparison with 1972 stock calculations (MOE, 1974, Section B), indicates a smaller ammonia stock, as already indicated by the seasonal curves, and comparable values for nitrate and total phosphorus. Nitrate was generally higher in 1975 than in 1972, except in August when the values were comparable (see also Figure 9).

PHOSPHORUS

Monthly means for total and soluble phosphorus in 1975 are compared with 1967-74 data in Tables 6 and 7. Separate results for 1975 are given for the weekly 4-station and monthly 8-station sampling runs. No significant trend for total or soluble phosphorus has occurred in the period 1968

to 1975, considering the large variability in the results (standard deviations are 25 to 100 percent of the means). The apparent decreased values for soluble phosphorus in July-August 1974 compared to previous or subsequent data are probably not significant, as they represent data taken from samples which were not frozen in the field (MOE, 1975). In addition, soluble phosphorus in 1975 showed large random variations from week to week; surface means were less than 0.003 mg/l on June 4, July 9 and 16, and August 19, 1975. As the harbour was only sampled three times in 1974, the mean values obtained for that year are obviously not representative of average conditions.

Seasonal variation of these parameters does not show any trends. Analysis of variance was performed on surface, mid-depth and bottom samples collected at the 4 main sampling locations between April 22 and September 9, 1975. Variations in total phosphorus were not significant at the 5 percent level with respect to any of depth, station or date. Although results for soluble phosphorus were frequently higher at the bottom than at the surface (Figure 12), this variation, as well as the between station variation, was not significant at the 5 percent level. Variations of soluble phosphorus with sampling date were significant at the 0.5 percent level; however, no seasonal trend is visible, with low values occurring on widely scattered dates, as mentioned above (see Figure 12). Such variations are not correlated with any other chemical parameters or with biological activity; indeed, two dates of low dissolved phosphorus (June 4 and July 16) represent a below average and one of the highest levels of chlorophyll a, respectively.

One of the effects of hypolimnetic anoxia is the reduction of insoluble ferric iron to the relatively soluble ferrous state (Stumm and Morgan, 1970; Mortimer, 1974; MOE, 1974, Section C). As phosphorus is held in an adsorbed or precipitated form on ferric hydroxide, reduction of iron should result in the liberation of soluble phosphate. The highest bottom values of dissolved phosphorus in 1975 (0.11 and 0.12 mg/l) were recorded on May 21 and July 9 at station 252, in relatively shallow water. Although these readings coincided with high iron results (0.65 and 1.3 mg/l), dissolved oxygen was low on only July 9.

The highest 3-station (4, 258, 270) bottom means for dissolved phosphorus were 0.040, 0.031 and 0.034 mg/l observed on June 11, June 25 and July 23, respectively. The June data were obtained at a time of approach to bottom anoxia (June 25 bottom DO values were below 1 mg/l), while the July figure

derives from an increased DO value (4.3 mg/l), presumably resulting from the mixing experiment. All these figures were obtained under conditions of low bottom iron values (0.15 to 0.20 mg/l). As observed in 1972, little relationship exists in Hamilton Harbour between low dissolved oxygen and increased soluble phosphorus or iron figures.

Unlike the conclusion of Harris (1976), we find little evidence for soluble phosphorus release from the sediments. Our computations of the means for his June 30 and July 7 data are 0.008 and 0.095 mg/l, not 0.044 and 0.053 used in Harris's report. The mean phosphorus values for August 25 are strongly affected by one reading of 0.0085 mg/l at Station 270. If this reading is omitted in the averaging and the recomputed means for June 30 and July 7 are used, there appears to be little effect from bottom anoxia on phosphorus levels between late June and September.

An additional discrepancy between Harris's data and ours was that he obtained large variations in surface soluble phosphorus in September and October (averages as high as 0.060 mg/l; our averages were never above 0.015 mg/l for this period). Such differences may be due to the known difficulty in preserving soluble phosphorus samples, other than that, no explanation can be given for this discrepancy.

That the control of phosphorus release from sediments may be more complicated than the simple iron-phosphorus-DO system was suggested by the R-mode factor analysis of June and August sediment samples (section C, sediment chemistry). Sediment total phosphorus was found to be related to zinc, lead, manganese, cadmium, mercury, aluminum, and organic content, as measured by loss on ignition. This could be a manifestation of physical (particulate P being carried to deep water areas by the currents) as well as chemical (precipitation by Al or adsorption) control on phosphorus deposition and release. More experimental work would be helpful on this point.

Although anoxic conditions were achieved at the sediment-water interface, the redox potential in a microlayer next to the water may not have dropped sufficiently low to liberate ferrous iron and phosphate. Redox potential measurements were not obtained near the sediment-water interface of the deepest stations (4 and 258) due to instrumentation limitations. At station 270, zero potentials were seen at the bottom around the end of June and again during August. However, it is impossible to ascertain the exact location of the probe with respect to the sediment-water interface, and the probe may have been indicating more severely reducing conditions from several centimeters below the true interface. Mechanical

disturbance of the interface by the sensor module may also have occurred. In addition, sulfide may have produced variable effects (see redox potential discussion); this is evident from the abnormally low redox potential values measured in the water column. The mean sulfide content of the surface portion of August sediment samples was 370 ug/g, with a maximum value of 2600 ug/g being obtained at station 262 (Randle's Reef). Certainly, in situ measurement of detailed redox potential variations in an interface ten or more meters from the surface is a difficult task more appropriately performed in the laboratory. At any rate, the anoxic tank experiment of Mortimer (1941) indicates a time lag of approximately six weeks from the establishment of anoxia to the liberation of iron and phosphorus. If this result can be applied to Hamilton Harbour, the liberation of these substances is not seen because mixing relieved the condition of bottom anoxia after only about five weeks. It would be valuable to obtain a bulk sediment sample and monitor redox potential and chemical variations at the sediment-water interface for extended periods of anoxia.

SILICA

Harbour-wide surface and bottom means of silica for 1975 are plotted as a function of sampling date in Figure 13, and in isopleth form in Figure 14. Values have decreased from a spring maximum of 1.4 mg/l Si (surface) and 1.3 mg/l (bottom) to an early July minimum of 0.15 mg/l (surface) and 0.4 mg/l (bottom). With the onset of summer stratification in late May, surface waters became depleted in silica compared to bottom waters, although the Si concentration of both layers decreased in May and June. Presumably as a result of the artificial mixing experiment, silica was distributed almost uniformly throughout the water column on July 16-23 and again on August 6. After the number of air lines operating in the harbour was reduced to one, depth stratification of silica set in again (September), and persisted until overturn (early October).

The surface and bottom mean silica concentrations were 0.7 and 0.8 mg/l Si, respectively. Other typical results for the Great Lakes indicate concentrations of 1.0-1.2 mg/l Si in Lake Superior and 0.02 to 0.2 mg/l Si in Lake Erie (Dobson, Gilbertson and Sly, 1974) and 0.12 and 0.20 mg/l Si in the surface and bottom of Lake Ontario (Shiomi and Chawla, 1970). Although Dobson et al (1974) stated that the lower silica concentration in Lake Erie relative to Lake Superior is related to the eutrophic status of Lake Erie (because of uptake of silica by phytoplankton, particularly diatoms), the hydrogeological characteristics of the various

watersheds must play a role in determining silica concentrations. Silica is generally derived from the decomposition of aluminosilicate minerals in the drainage basin from which the waters originate (Hutchinson, 1957). In addition, silica is thought to enter the hypolimnion of deoxygenated stratified lakes as a result of the reduction of ferric and manganese oxides and consequent release of coprecipitated silica from the bottom sediments (Kato, 1969).

The seasonal and depth dependence of silica concentration in Hamilton Harbour is similar to that in Lake Ontario (Shiomi and Chawla, 1970). Unlike Lake Ontario, however, the silica concentration curve does not correlate with those of nitrate and soluble phosphate. They suggest that concentrations of these nutrients were related to diatom growth in Lake Ontario; removal by diatoms is cited as the most important mechanism of silica removal (Hutchinson, 1957, chapter 14). Among other factors such as temperature and light penetration, the silica content of Hamilton Harbour is limiting diatom growth in Hamilton Harbour, while the other nutrients are present in large excess as a result of discharges. As a spring growth of diatoms occurred in Hamilton Harbour, it is felt that phytoplankton growth in the epilimnion is the dominant factor in producing the observed seasonal dependence and depth stratification of silica concentration.

HEAVY METALS

As part of the 1975 sampling survey, depth composite samples were taken at the four sampling stations and analyzed for nickel, cobalt, manganese, chromium, copper, zinc, cadmium, mercury, lead and molybdenum. The purpose of these tests was to determine whether any metal was present in amounts sufficient to present a toxicity problem to the biota. In addition, weekly samples from all stations and depths were analyzed for iron.

Results for nickel, cobalt, chromium, cadmium and molybdenum indicated that Hamilton Harbour contains less than minimum detectable amounts of 0.01-0.05 mg/l in nearly all samples. These metals are therefore not considered a problem (unless they happen to actually be limiting the growth of a species for which any one could be an essential minor nutrient). They will not be discussed further.

Harbour-wide means of monthly data are given for the other metals in Table 8. Except for manganese, the concentrations showed no significant spatial distribution. In the June-September period, manganese results for stations 4 and 258 were significantly greater than those for stations 252 and 270. Results for zinc are in the range which is sufficient to suppress phytoplankton growth (Harris, 1976). For further elucidation of possible algicidal effect, zinc is to be measured on all samples in 1976.

The only heavy metal measured in the 1972 survey was iron. Results for iron in 1975, as in 1972, are highly variable. Surface and bottom means were 0.27 and 0.36 mg/l, with standard deviations of 0.21 and 0.24 mg/l for the period April 30 - September 9, 1975. Depth-time distributions of iron are given in Figure 15.

Under anoxic conditions, iron is reduced to the ferrous state (Mortimer, 1941) and appears in increased quantity in soluble form. At a redox potential of zero and a pH of 7, which represents highly anoxic conditions generally found only within a few centimeters of the mud-water interface, the solubility of Fe^{2+} is only 10^{-6} M (0.06 mg/l). During 1975, redox potential values below 50 mv were recorded only at station 270, from June 25 to July 9, and August 12 to September 16, 1975 (Figure 2). The intervening period was one in which the largest air flow from the aerators was occurring. As mentioned earlier, much of the iron in Hamilton Harbour water may be held as organic complexes, which are quite resistant to oxidation and may actually reduce ferric iron to ferrous (Theis and Singer, 1973, 1974). It is felt that no reliable redox potential measurements were obtained for the mud-water interface, and it is possible that the interface did not become sufficiently reducing to liberate large quantities of iron. Only in the mid-August to mid-September period is there evidence of iron being liberated from the sediments. At this time, bottom iron values rose to an average of 0.6 mg/l compared with surface values of about 0.3 mg/l.

Manganese is reduced to the soluble divalent state and released to the water column at a higher potential than required for iron reduction (Stumm and Morgan, 1970; Hutchinson, 1957). Although it cannot be proven, due to the lack of individual depth samples, the spatial and temporal distribution of manganese suggests that it was released from the sediment in deep areas during times of anoxia or near-anoxia in 1975.

MINERAL CHEMISTRY

The chemical characteristics of any natural water body are governed by its interactions with the lithosphere and atmosphere. As such, models have been developed involving equilibria of minerals such as calcite, dolomite, apatite, kaolinite, gibbsite, Na- and K-feldspars with water and atmospheric carbon dioxide. Although natural waters exist in a dynamic condition due to such factors as thermal stratification, mixing of different water bodies, biological activity, etc., such models may be used to indicate general

chemical tendencies within the water bodies. The composition of the Great Lakes has been discussed in terms of equilibrium models (Kramer, 1964, 1967).

In a confined water body which has been modified greatly by man's activities, such as Hamilton Harbour, equilibrium models may be used to indicate the effect of man's activities on the water chemistry, and estimate the existing departure from equilibrium conditions.

Kramer (1964) has built up a model of Great Lakes water chemistry involving equilibrium controls of calcium, magnesium, sodium, potassium, silica, phosphorus, and fluoride concentrations and pH. Sulfate and chloride are considered with respect to their contribution to electroneutrality; however, no equilibrium controls exist at the concentrations of these ions normally present in fresh water. Although calculations on a similar model could be performed for Hamilton Harbour, these are beyond the scope of the present study. Several solubility relationships among Hamilton Harbour data will, however, be discussed, and the conductivity of Hamilton Harbour water will be discussed in terms of its ionic components.

Kramer (1967) has discussed equilibria of Great Lakes water with calcium carbonate, dolomite, and several silicates. These will be applied to Hamilton Harbour water using surface samples taken on four dates during the 1975 sampling program.

In Figures 16 and 17, the saturation of Hamilton Harbour water with respect to calcite and dolomite is explored. The general trend observed by Kramer (1967) was that of unsaturation during the winter and supersaturation in summer (epilimnetic) samples. In Hamilton Harbour, much more scatter was observed with most data points lying outside the range observed by Kramer. With the exception of one point (station 4 on April 22) all Hamilton Harbour samples checked were supersaturated with respect to both minerals. The values of the ion products are highly dependent upon pH, and as this parameter may change by several tenths of a unit between samples and measurement (all pH values were done in the lab), changes in this parameter may account for the observed results. In addition, the pH is strongly affected by biological activity in the productive Hamilton Harbour waters. Low pH on September 9 (and consequent reduced degree of supersaturation with respect to calcite and dolomite) may have resulted from decomposition of dead phytoplankton and decay of other organic matter, as this date was in a period of low chlorophyll a values. Absorption of acidic fumes from the air may also be important in this highly industrialized area. At any rate, the increased degree of supersaturation generally observed indicates the effect of man's activities on Hamilton Harbour mineral chemistry.

Silicate equilibria may be depicted in terms of plots of (pH-pNa), (2 pH-pCa), or (pH-pK) against pSi (Stumm and Morgan, 1970, chapter 8; Kramer, 1967) see Figure 18. In the early spring, pSi is 4 to 4.5, (pH-pNa) is 5 to 6 and (pH-pK) is 4 to 5. These results lie in the region of kaolinite stability (but near the gibbsite-kaolinite boundary), suggesting that Hamilton Harbour water is in equilibrium with this mineral in the sediments during time of complete mixing. During stratification, silica concentration is thought to be controlled by biological uptake (see section on silica chemistry).

Values for (2 pH-pCa) lie in the range 13 to 14.5. Although mainly in the kaolinite field, the upper end of this range is on the kaolinite - Ca-feldspar boundary. Overall, Hamilton Harbour water appears to be stable with respect to kaolinite. This is reasonable considering the fact that kaolinite has been found to occur as a major phase in bottom sediments of the Great Lakes (Kramer, 1967).

CONDUCTIVITY MODEL

As the conductivity of a water sample is directly related to the concentration of dissolved ionic salts, the overall accuracy of mineral analyses may be verified by computing the conductivity of the water, in addition to the usual ionic balance (electroneutrality) relationship.

The conductivity of a dilute salt solution may be calculated from the concentrations of the individual ions, their ionic charges, and the equivalent conductance of the ions at infinite dilution. The relationship used (Rossum, 1975) was originally developed by Onsager, and is as follows:

$$G = \Lambda_0 C - (K_1 \Lambda_0 + K_2) C^{1.5} \quad (1)$$

where

G = conductivity
 Λ_0 = equivalent conductance of the salt at infinite dilution
C = concentration of the salt solution
 K_1 and K_2 = constants that are associated with the relaxation of the ion-cloud and electrophoretic effects relative to ion mobility.

The first term represents the conductivity G_0 which the water would have if ionic interaction effects (ion-cloud and electrophoretic) could be ignored, i.e. if each ion behaved as a separate entity. It is calculated separately for negative and positive ions and summed as follows:

$$G_o = \sum c_- \zeta_- + \sum c_+ \zeta_+ \quad (2)$$

where

c_- and c_+ are concentrations (milliequivalents per liter) of negative and positive ions;
 ζ_- and ζ_+ are equivalent ionic conductances at infinite dilution.

The summation is carried out over all ionic species present in the solution.

The second term represents a correction for the above-mentioned interionic effects. The values of K_1 and K_2 in Equation (1) are calculated from the temperature, viscosity and dielectric constant of water, as well as the valence and equivalent conductance of each ion. An expansion of this term, and the equivalent conductances of the major ions at infinite dilution are given by Rossum (1975) and will not be repeated here.

This model was verified by computing conductivities of NaCl, KCl, Na₂SO₄ and MgSO₄ solutions, and comparing the results with observed data for KCl (APHA, 1965) and data estimated from a conductivity - ionic strength relationship as well as calculations involving a simpler model also based on the Onsager relationship (Lind, 1970). Results are given in Table 9. This model gives results which are within 1 percent of the figures for NaCl, KCl and Na₂SO₄. With MgSO₄, the model produces a closer fit to estimated data than the simpler model; however, figures are still 14 to 24 percent high in the 0.001-0.01 N concentration range. This discrepancy is believed to be due to ion-pair formation, the effect of which is neglected in the model. More is said about this subsequently.

Monthly surface data from four sampling stations in Hamilton Harbour were analyzed using this model. Individual samples were analyzed for three dates; harbour-wide means were analyzed for all monthly samples. The justification for use of harbour-wide means is that the spatial variation of the principal ionic components (Table 10) is either not significant or only weakly significant on the basis of a two-way analysis of variance. The results so obtained are given in Table 11.

Assuming the contribution from other bases is negligible, the alkalinity was broken down into carbonate and bicarbonate concentrations according to pH as follows:

$$[\text{alk}] = [\text{CO}_3^{=}] + \frac{1}{2}[\text{HCO}_3^-] \quad (3)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{=}]}{[\text{HCO}_3^-]} \quad (4)$$

In these equations, all species are expressed in molar concentrations and K_2 is the second ionization constant of carbonic acid. Values for K_2 at the observed temperature of each sample were obtained from Stumm and Morgan (1970), and activity effects were neglected. At the average pH of the samples (8.2), ammonia-nitrogen is 90 percent in the NH_4^+ form (the rest is un-ionized NH_3). This fact was used in calculating the NH_4^+ ionic concentration from observed $\text{NH}_3\text{-N}$ data.

For comparison purposes, average Lake Ontario data (IJC, 1969, p. 70,82,93) were also analyzed. Figures for all ions but nitrate and ammonium were corrected for the estimated rate of change from 1966 to 1975 as stated on p. 93; carbonate was estimated from bicarbonate assuming an average surface pH of 8.5 (IJC, 1969, p. 104).

Computed ionic balances and conductivities for these conditions are given in Table 11. Deviations of ionic concentrations from the exact balance required by electroneutrality range from 1 to 8 percent in random direction. Errors of this magnitude are larger than expected and tend to indicate lack of accuracy in the analysis for one or more constituents. Inspection of the data shows that chloride and sulfate concentrations for April to June samples were reported only to a precision of ± 5 mg/l. An error of this magnitude in both chloride and sulfate is large enough to account for the observed errors on April 22 individual samples; it is suggested that all chloride and sulfate analyses be reported to a precision of ± 1 mg/l or better.

All but one of the calculated conductivity values are high by 6 to 12 percent, an improbably high error. However, the conductivity model neglects ion-pair formation. The following equilibrium constants for ion-pair formation are available (Sillen and Martell, 1964):



The Hamilton Harbour results were checked to see whether complex formation might be important. By rough calculations involving only one equilibrium at a time, it was seen that about 15 percent of the Ca and 30 percent of the SO_4 are

associated by equilibrium (8). About 2 percent of the Ca and HCO_3 are complexed by equilibrium (10). Equilibrium (9) is also important, but exact calculation of the effects of these equilibria would require development of a complete equilibrium model accounting for all reactions together, plus electroneutrality. Such a project is not warranted at this time.

The effect of ion-pair formation on the calculated conductivity of MgSO_4 solutions according to equilibrium (9) was investigated. This results in an over-compensation at the 0.01 N concentration level. The reason for this could be the fact that the equilibrium constant for reaction (9) was measured at 18°C and the conductivity figures are for 25°. Alternately, experimental error in the measurement of the constant or decreased accuracy of the model at high concentrations could have an effect. At any rate, this calculation indicates the potential magnitude of errors in the model resulting from ion-pair formation.

As equilibrium (8) (CaSO_4 formation) appears to have the greatest effect in Hamilton Harbour, and the complex formed is electrically neutral (thus not contributing to conductivity), its effect was checked using the data for April 22 and May 29, 1975. The results obtained were 530 and 549 umho/cm, compared to observed results of 538 and 525 umho/cm. Thus a closer agreement with observed data is obtained. The remaining variations are likely the result of analytical errors, as evidenced by the deviations in ionic balances already mentioned.

The comparison of Hamilton Harbour water with Lake Ontario indicates that all ions except calcium and bicarbonate are present in Hamilton Harbour at about twice the concentration of Lake Ontario, or higher. Carbonate is not compared, as its concentration is very low at the prevailing pH, and at any rate is highly pH-dependent. A considerable buildup in the concentrations of the major ions since 1910 has been noted for the Great Lakes, except Lake Superior (IJC, 1969). Chloride and sulfate have been especially affected. As these ions are added in municipal and industrial wastewater effluents and runoff from road salting, the more polluted a water is, the greater is the contribution of these ions to conductivity. This is reflected in the fact that the contribution of these ions to conductivity for Hamilton Harbour according to the average of the figures of Table 11 is 36% for Hamilton Harbour, compared to 29% for Lake Ontario, and 22% for the mean world composition of river water (Livingston, 1963). The Hamilton Harbour figures thus are as expected considering the major use of Hamilton Harbour as a receiving water for industrial and municipal wastes. Calcium ion

concentration is controlled by the calcite and dolomite equilibria already discussed; bicarbonate is controlled by the equilibrium between atmospheric and dissolved carbon dioxide. (Average observed results indicate slight supersaturation of dissolved carbon dioxide in both Lake Ontario and Hamilton Harbour except at the highest observed pH's; see Stumm and Morgan, 1970, p. 127).

Table 11 also indicates an estimate of the contribution of each ionic species to the calculated conductivity. These were obtained from the relation:

$$g = c \zeta (G_0/G)$$

were

g is the ionic conductivity for any ion

c and ζ are the concentration (meq/l) and equivalent conductance at infinite dilution for that ion

G_0 and G are as defined in equations (2) and (1)

For most samples, chloride is the greatest anionic contributor to conductivity, followed closely by sulfate and bicarbonate. Calcium is the greatest cationic contributor to conductivity.

The main interest in evaluating ionic contributors to conductivity is the portion of conductivity due to non-conservative (biologically active) substances. This is important since the numerical model (MOE, 1974, section E) is currently programmed only for conservative materials (total dissolved solids, as estimated from conductivity). If the non-conservatives are represented by the nitrogen parameters (ammonia and nitrate), the results of Table 11 indicate that non-conservative materials contribute 2 to 3 percent of the total conductivity. This figure is in good agreement with the average result of 2 percent biodegradability observed on 5-day incubation of a series of Hamilton Harbour samples collected in 1974.

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TABLE 1: Dissolved Oxygen Stocks, 1975

Date	Method(a)	DO Stock, 10 ⁶ kg		Min 5 mg/l DO
		Method(b)	Method(c)	
May 2	2.704	2.646	2.606	2.646
June 3	1.964	1.998	1.948	2.018
July 14	1.077	1.016	1.005	1.564
Aug 12	0.972	0.946	0.927	1.592
Sep 16	1.458	1.312	1.293	1.652

Note:

Method(a) is the integration of observed DO-depth profiles from the surface to the average sounding of each station.

Method(b) is the calculation of DO stocks for six vertical zones per station from average observed DO in each zone.

Method(c) is the calculation of DO stocks for six vertical zones per station from DO values calculated from the surface DO for each station and the harbour-wide average DO-depth profile.

Min 5 mg/l refers to the DO stock which would be present if the DO were at least 5 mg/l throughout the harbour. It was calculated using method(b) except that if the average DO for a zone was below 5 mg/l, 5.0 mg/l was used instead.

TABLE 2: Estimated Oxygen Depletion Rates,
Hamilton Harbour, 1975

	<u>Station 4</u>	<u>Station 258</u>	<u>Station 270</u>
Jun 4-Jun 11	0.065	0.055	0.021
Jun 11-Jun 25	0.160	0.166	0.033
Jun (Harris, 1976) (average)	0.05-0.07		

All rates given in $\text{g/m}^2\text{-hr.}$

TABLE 3

AMMONIA SURFACE DATA, 1966-1975

(a) June-October averages for each station

	<u>Station</u>						
	<u>20</u>	<u>256</u>	<u>257</u>	<u>258</u>	<u>262</u>	<u>265</u>	<u>269</u>
1966	7.3	5.5	3.5	3.4	3.7	3.3	4.2
1967	3.1	3.9	2.4	2.4	3.3	2.8	2.2
1968	5.3	5.3	3.7	3.0	4.6	4.1	3.8
1969	4.7	5.1	3.5	3.4	4.7	3.5	3.1
1970	7.8	7.7	7.0	6.3	8.3	5.9	6.9
1971	7.4	5.8	4.9	5.3	8.5	4.8	5.0
1972	2.6	2.0	1.3	1.6	2.8	1.2	1.7
1974	0.50	0.10	0.17	0.21	0.24	0.19	---
1975	3.5	1.4	1.1	1.1	1.1	0.9	1.3

(b) Monthly and annual averages for entire bay

	<u>June</u>	<u>July</u>	<u>Aug.</u>	<u>Sept.</u>	<u>Oct.</u>	<u>Year</u>
1966	6.0	4.2	3.6	3.1	4.7	4.4
1967	3.8	2.3	2.6	2.2	2.4	2.8
1968	6.8	4.7	3.4	3.0	3.1	4.3
1969	4.9	4.0	1.9	3.3	5.5	4.0
1970	8.9	6.8	7.3	6.4	3.5	6.9
1971	9.3	6.1	4.7	3.7	---	5.9
1972	---	2.4	1.9	1.6	1.5	1.9
1974	---	0.016	0.30	---	0.42	0.26
1975*	1.9	1.2	0.33	0.47	0.36	0.85
#	2.7	1.5	0.91	0.94	0.66	1.4

Note: All figures are in mg/l as N

Analytical Precision \pm about 10%

Standard deviations of above figures (including station and time variations) are generally 30-50% of the means.

* 4-station weekly surveys

8-station monthly surveys

TABLE 4

NITRATE SURFACE DATA, 1966-1975

(a) June-October averages for each station

	<u>Station</u>						
	<u>20</u>	<u>256</u>	<u>257</u>	<u>258</u>	<u>262</u>	<u>265</u>	<u>269</u>
1966	0.93	1.25	1.27	1.03	1.01	1.20	1.11
1967	2.48	2.62	2.79	2.89	2.59	2.74	2.78
1968	0.95	1.13	1.38	1.27	1.31	1.30	1.19
1969	1.11	1.28	1.47	1.43	1.45	1.36	1.38
1970	1.36	1.45	1.99	1.85	1.84	1.81	1.73
1971	1.52	1.92	2.15	2.10	2.07	2.08	2.00
1972	1.27	1.64	1.70	1.78	1.71	1.73	1.61
1974	3.7	2.9	2.3	1.9	3.0	2.3	----
1975	1.87	1.88	1.81	1.86	1.89	1.91	1.88

(b) Monthly and annual average for entire bay

	<u>June</u>	<u>July</u>	<u>Aug.</u>	<u>Sept.</u>	<u>Oct.</u>	<u>Year</u>
1966	----	----	1.10	1.41	0.56	1.11
1967	1.30	3.84	3.95	1.85	1.16	2.7
1968	0.62	1.85	1.61	1.06	0.85	1.22
1969	0.84	1.82	1.69	1.34	0.94	1.35
1970	0.87	2.40	1.90	1.64	1.99	1.75
1971	1.42	2.22	2.18	1.50	----	1.97
1972	----	1.89	1.77	1.42	1.58	1.65
1974	----	2.6	3.5	----	2.5	2.9
1975*	1.81	2.04	2.05	1.90	1.82	1.92
#	1.30	2.55	2.03	1.74	1.67	1.86

Note: All figures are in mg/l as N

Analytical Precision \pm about 10%

Standard deviations of above figures (including station and date variations) are generally 30-50% of station means and 20-50% of monthly means.

* 4-station weekly surveys

8-station monthly surveys

TABLE 5

NUTRIENT STOCKS, HAMILTON HARBOUR, 1975

	<u>May 2</u>	<u>June 3</u>	<u>July 14</u>	<u>Aug. 12</u>	<u>Sept. 16</u>	<u>Oct. 17</u>
NH ₃ (10 ⁵ kg)	7.90	9.17	2.36	1.14	1.29	1.58
TKN (10 ⁵ kg)	9.40	10.40	4.58	3.91	2.53	3.58
NO ₂ (10 ⁵ kg)	0.34	0.46	0.40	0.29	0.22	0.93
NO ₃ (10 ⁵ kg)	3.62	3.23	5.05	4.42	3.39	4.90
Total P (10 ³ kg)	18.6	18.0	14.0	14.9	10.8	15.7
Soluble P (10 ³ kg)	5.4	6.0	3.7	3.4	4.7	5.9
Chlorophyll <u>a</u> (10 ³ kg)	---	3.74	5.30	3.88	3.22	1.26
Chlorophyll <u>b</u> (10 ³ kg)	---	0.44	1.16	0.84	0.48	0.22

TABLE 6

TOTAL PHOSPHORUS SURFACE DATA, 1967-1975

(a) June-October averages for each station

	<u>Station</u>						
	<u>20</u>	<u>256</u>	<u>257</u>	<u>258</u>	<u>262</u>	<u>265</u>	<u>269</u>
1967	.112	.091	.087	.067	.077	.103	.126
1968	.099	.060	.034	.035	.050	.092	.048
1969	.093	.084	.044	.043	.049	.061	.067
1970	.275**	.074	.036	.044	.054	.046	.065
1971	.279	.055	.033	.031	.037	.037	.040
1972	.172	.086	.072	.068	.065	.068	.078
1974	.088	.077	.052	.057	.065	.066	---
1975	.122	.072	.082	.054	.066	.058	.059

(b) Monthly and annual averages for entire bay

	<u>June</u>	<u>July</u>	<u>Aug.</u>	<u>Sept.</u>	<u>Oct.</u>	<u>Year</u>
1967	.075	.081	.107	.120	.102	.095
1968	.048	.060	.058	.075	.068	.060
1969	.058	.048	.037	.087	.094	.063
1970	.099**	.091	.065	.078	.059	.078
1971	.091	.055	.072	.098	---	.073
1972	---	.087	.082	.088	.093	.088
1974	---	.067	.102	---	.057	.084
1975*	.082	.086	.069	.077	.063	.075
#	.084	.074	.082	.050	.069	.072

Note: All figures are in mg/l as P

**One questionably high value was omitted

Analytical Precision \pm 0.003 mg/l or 10%, whichever is greater.
 Standard deviations of above figures (including station and date variations) are generally 50-100% of the means.

* 4-station weekly surveys
 # 8-station monthly surveys

TABLE 7

SOLUBLE PHOSPHORUS SURFACE DATA, 1967-1975

(a) June-October averages for each station

	<u>Station</u>						
	<u>20</u>	<u>256</u>	<u>257</u>	<u>258</u>	<u>262</u>	<u>265</u>	<u>269</u>
1967	.060	.060	.058	.056	.114	.100	.098
1968	.067	.023	.025	.022	.028	.047	.035
1969	.045	.041	.021	.027	.029	.031	.032
1970	.150**	.007	.016	.020	.013	.013	.013
1971	.101	.009	.004	.007	.004	.007	.012
1972	.057	.020	.017	.015	.016	.015	.020
1974	.016	.005	.002	.004	.010	.003	---
1975	.063	.016	.018	.016	.017	.014	.019

(b) Monthly and annual averages for entire bay

	<u>June</u>	<u>July</u>	<u>Aug.</u>	<u>Sept.</u>	<u>Oct.</u>	<u>Year</u>
1967	.054	.058	.091	.080	.064	.075
1968	.033	.034	.037	.040	.040	.036
1969	.018	.023	.014	.040	.071	.052
1970	.056**	.036	.033	.013	.007	.029
1971	.039	.016	.026	.052	---	.029
1972	---	.016	.024	.035	.021	.024
1974	---	.002	.004	---	.017	.008
1975*	.014	.012	.007	.011	.010	.011
#	.027	.017	.017	.021	.029	.022

Note: All figures are in mg/l as P.

**One questionably high value was omitted.

Analytical Precision \pm 0.003 mg/l or 10%, whichever is greater. Standard deviations of above figures (including station and date variation) are generally 50-150% of the means.

* 4-station weekly surveys
 # 8-station monthly surveys

TABLE 8: Harbour-wide Monthly Means of Heavy Metal Concentration
Hamilton Harbour, 1975 (mg/l)

	Iron	Manganese	Copper	Zinc	Lead
April	0.31	0.10	0.03	0.08	0.01
May	0.19	0.06	0.02	0.08	0.05
June	0.22	0.07	0.02	0.02	0.04
July	0.34	0.08	0.02	0.08	0.01
August	0.26	0.10	0.03	0.07	<0.01
September	0.37	0.13	<0.01	0.03	<0.01

TABLE 9: Calculated Specific Conductances of Single Salt Solutions

Salt	Normality	Calculated (this model, G_o , equation (1))	Calculated (Lind, 1970)	Estimated from conductivity-ionic strength curve (Lind, 1970)
NaCl	0.001	124	126	125
	0.01	1175	1180	1180
KCl	0.001	147	-	147*
	0.01	1404	-	1413*
Na ₂ SO ₄	0.001	124	127	126
	0.01	1127	1210	1130
MgSO ₄	0.001	122 (113) #	130	107
	0.01	989 (695) #	1230	800

Note:

- * Measured (APHA, 1965, p. 282)
 # Calculated allowing for MgSO₄ ion-pair formation,
 with log K=2.2 (Sillen and Martell, 1964)

TABLE 10: Analysis of Variance
Conductivity and Principal Ionic Components,
Surface Samples, Hamilton Harbour, 1975

<u>Parameter</u>	<u>Station Variation</u>			<u>Date Variation</u>		
	<u>F</u>	<u>df</u>	<u>Significance</u>	<u>F</u>	<u>df</u>	<u>Significance</u>
Conductivity	3.27	3,18	NS	49.0	6,18	0.1%
Alkalinity	8.90	3,18	5%	93.1	6,18	0.1%
Na	8.27	3,15	NS	94.5	5,15	0.1%
Ca	0.29	3,15	NS	139.3	5,15	0.1%
Cl	14.1	3,18	5%	152.3	6,18	0.1%

TABLE 11: Contribution of Various Ions to Total Conductivity, Hamilton Harbour 1975

1. Discrete surface samples

Date	Sta.	CO ₃ ⁼		HCO ₃ ⁻		SO ₄ ⁼		Cl ⁻		NO ₃ ⁻		Ca ⁺⁺		Mg ⁺⁺		Na ⁺		K ⁺		NH ₄ ⁺		Σ anions		Σ cations		Conduct. (umho/cm)
		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	meq/l	meq/l	Calc.	Obs.	
Apr 22	4	0.24	1	132	84	65	94	65	121	6.8	7	59	153	11	42	34	65	5.8	10	3.8	14	5.47	5.70	590	560	
	252	0.76	2	132	84	60	87	60	113	6.6	7	58	150	11	42	31	59	5.5	9	2.4	9	5.24	5.43	562	520	
	258	0.94	2	131	84	60	87	60	113	6.6	7	59	153	11	42	31	59	5.5	9	2.4	9	5.23	5.48	564	530	
	270	0.94	2	131	83	60	87	60	113	6.5	7	58	150	13	49	31	59	5.5	9	2.3	9	5.23	5.59	568	540	
May 29	4	1.32	3	129	82	65	94	75	141	6.2	6	57	148	11	42	35	66	6.1	10	3.1	12	5.73	5.61	604	540	
	252	2.24	6	123	78	65	94	70	131	5.9	6	56	145	12	46	34	65	5.9	10	2.2	8	5.51	5.54	588	520	
	258	2.59	6	127	81	65	94	65	122	6.2	6	56	145	12	46	33	63	5.8	9	2.2	8	5.46	5.49	580	520	
	270	1.67	4	130	83	65	94	70	131	6.0	6	55	142	12	46	33	63	5.8	9	2.5	9	5.61	5.46	588	520	
Sep 9	4	0.52	1	101	65	47	69	47	90	8.8	9	46	121	10	39	24	46	4.5	7	0.02	<1	4.12	4.27	448	455	
	252	0.41	1	103	67	47	69	47	90	9.5	10	46	121	10	41	25	47	4.6	7	0.05	<1	4.16	4.34	453	455	
	258	0.34	1	105	68	47	69	45	86	9.3	9	47	124	10	41	23	45	4.4	7	0.35	1	4.14	4.35	448	440	
	270	0.35	1	108	70	45	66	45	86	8.7	9	47	124	10	41	23	44	4.2	7	0.32	1	4.13	4.33	448	440	

2. Harbour-wide means of surface samples

Apr 22	0.60	2	132	84	61	88	61	115	6.6	7	58.5	151	11.5	44	32	61	5.6	9	2.7	10	5.28	5.56	571	538
May 7	0.56	1	138	87	67	97	66	124	5.1	5	57	147	13	49	30	56	5.7	9	2.8	11	5.61	5.49	586	554
May 29	1.74	4	128	81	65	94	70	131	6.1	6	56	145	12	45	34	65	5.9	10	2.5	9	5.58	5.54	590	525
Jun 11	0.77	2	116	74	61	89	67	126	6.1	6	55	143	12	45	31	60	5.8	10	2.4	9	5.19	5.37	563	528
Aug 13	0.79	2	109	69	75	109	57	107	10.6	11	50.5	131	11	42	27	51	4.8	8	0.27	1	5.14	4.74	530	470
Sep 9	0.42	1	104	67	46	68	46	88	8.9	9	46.5	122	10	39	23.5	45	4.4	7	0.18	1	4.12	4.30	448	449

3. Lake Ontario, 1975 Estimate (IJC, 1969, p. 70,82,93)

	1.5	4	115	75	28.6	43	31.1	60	1.3	1	43.9	117	6.4	25	14.5	28	1.44	2	0.06	<1	3.43	3.39	356	331
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4. World mean river water composition (Livingstone, 1963).

	-	-	58.4	40	11.2	17	7.8	16	1.0	1	15	42	4.1	17	6.3	13	2.3	4	-	-	1.43	1.42	149	-
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Note: Columns "A" are concentration in mg/l of each ion as stated.
Columns "B" are ionic contributions to conductivity in umho/cm.



FIGURE 1: HAMILTON HARBOUR ARTIFICIAL MIXING SYSTEM & SAMPLING STATIONS

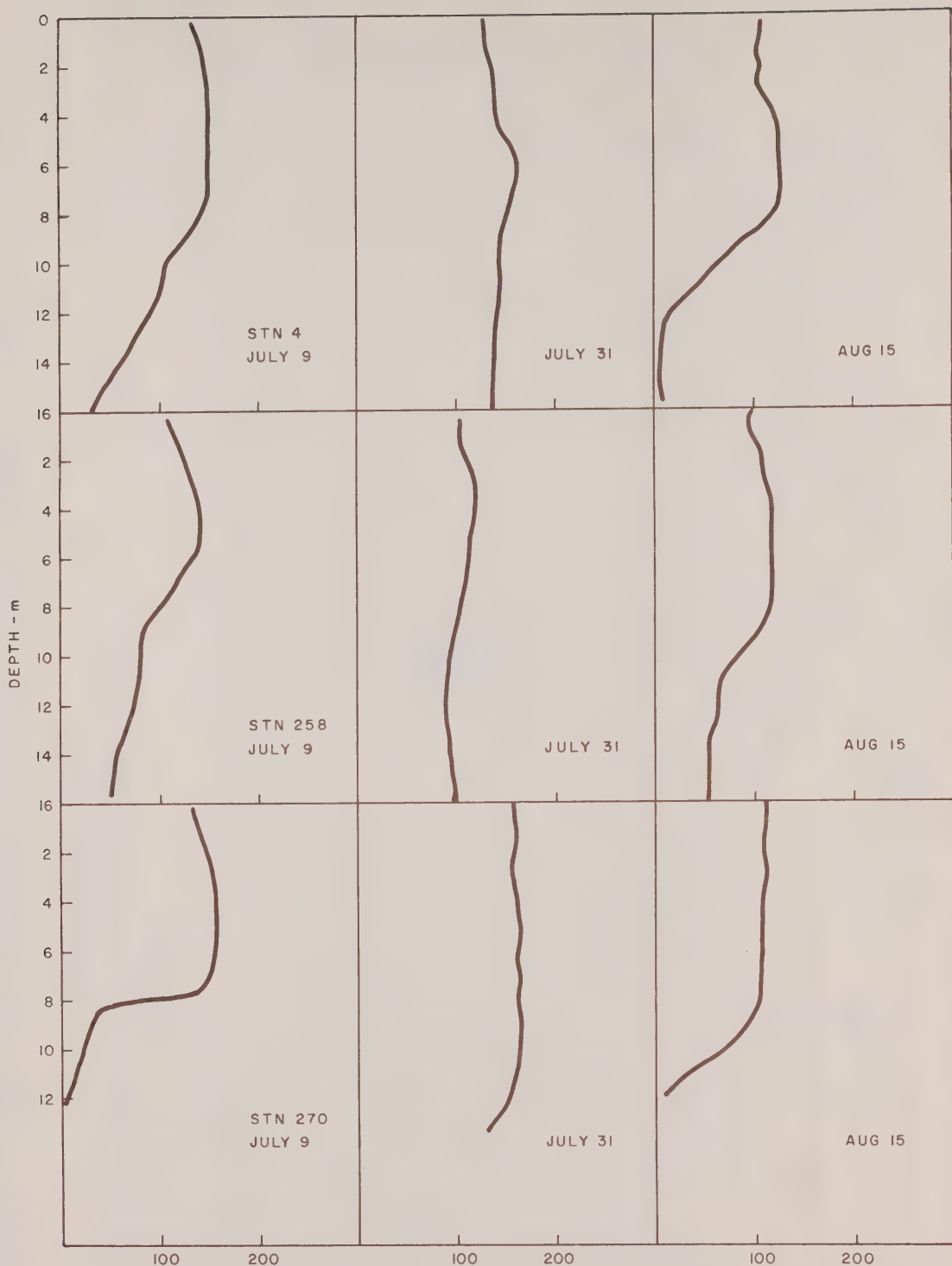


FIG. 2 REDOX POTENTIAL (mv) - DEPTH PROFILES DURING MIXING PERIOD. (1975)

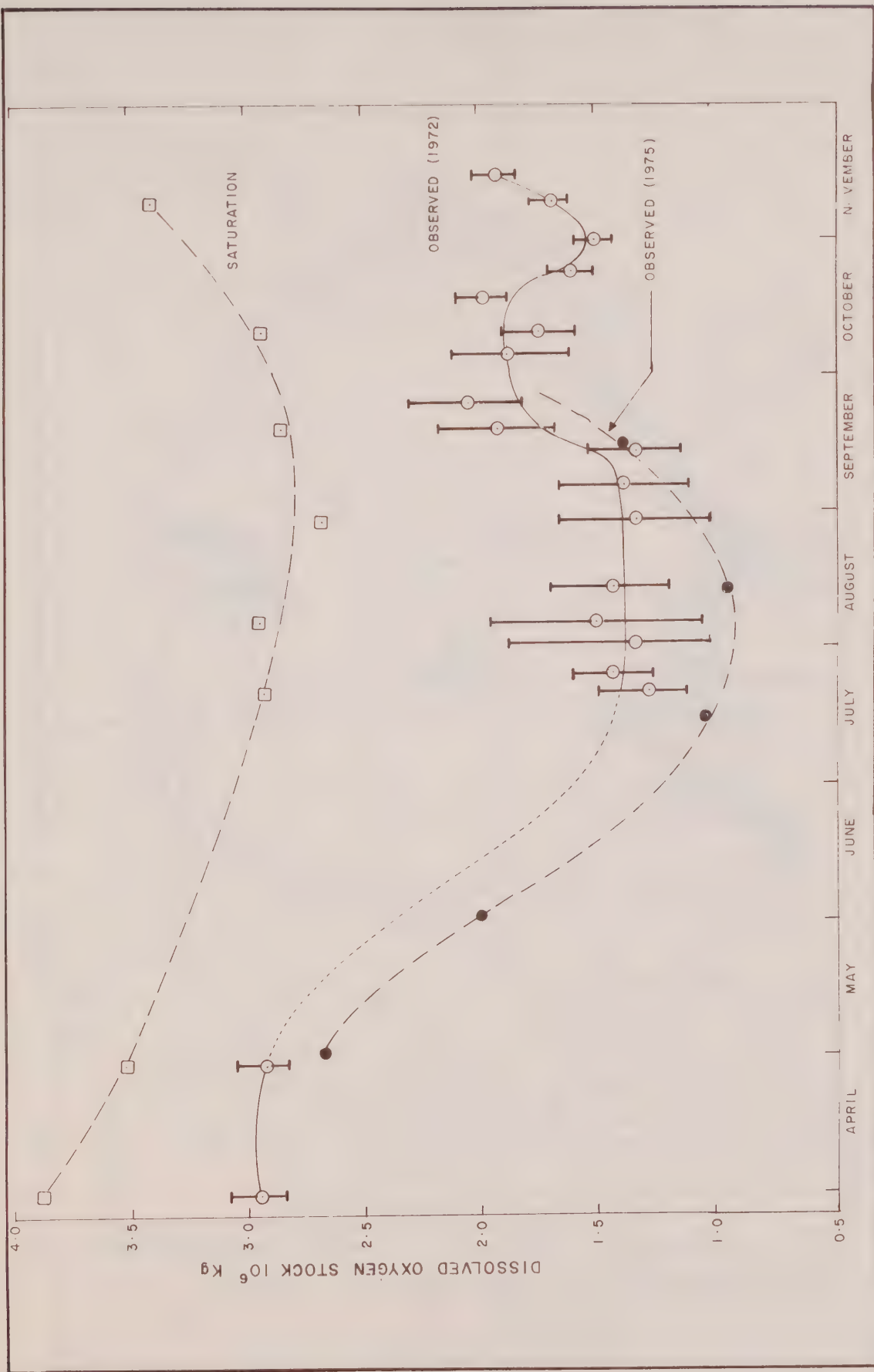


FIGURE 3: OBSERVED AND SATURATION DISSOLVED OXYGEN STOCK IN HAMILTON HARBOUR, 1972 AND 1975

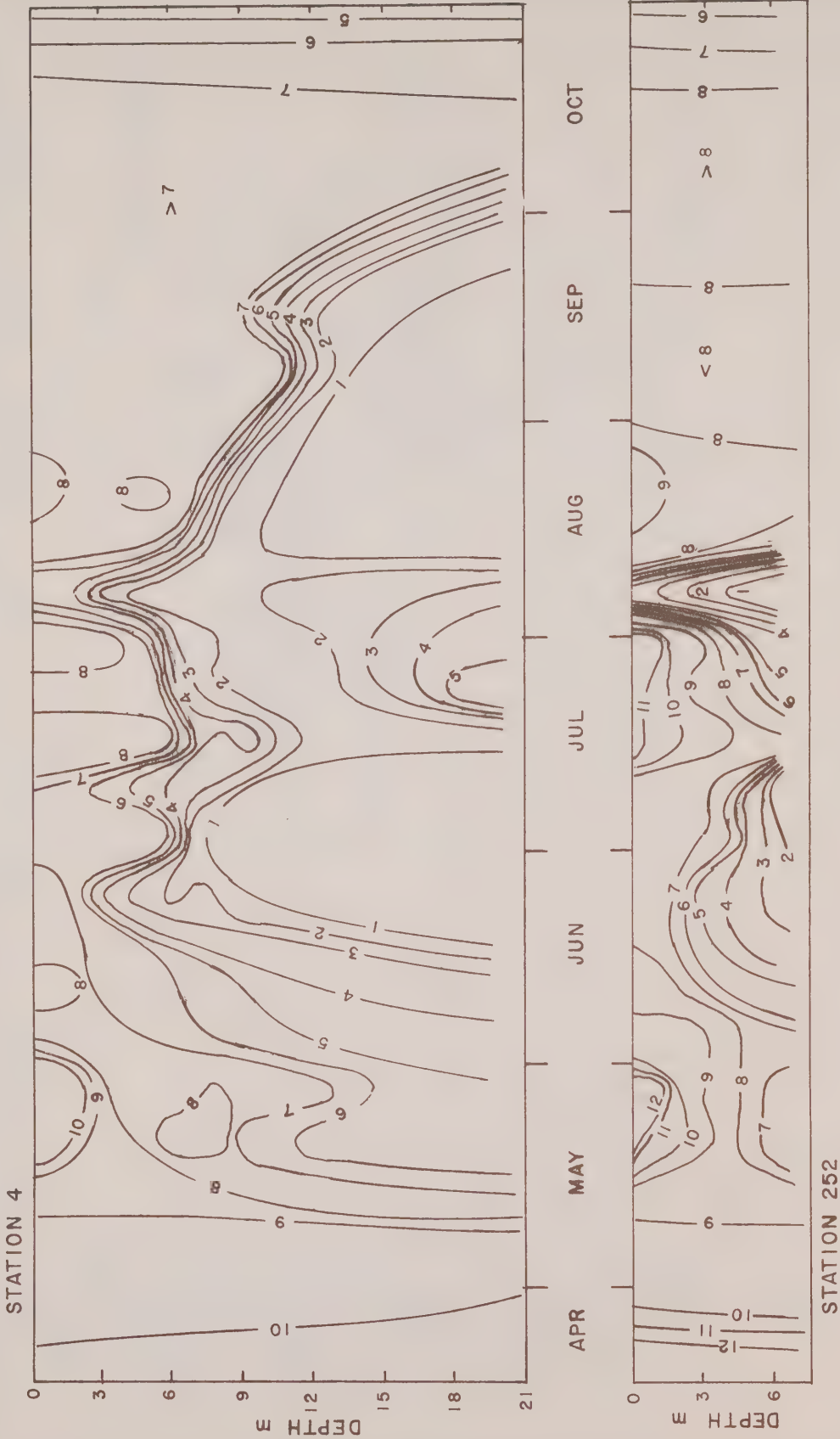


FIGURE 4: DISSOLVED OXYGEN ISOPLETHS (1975)

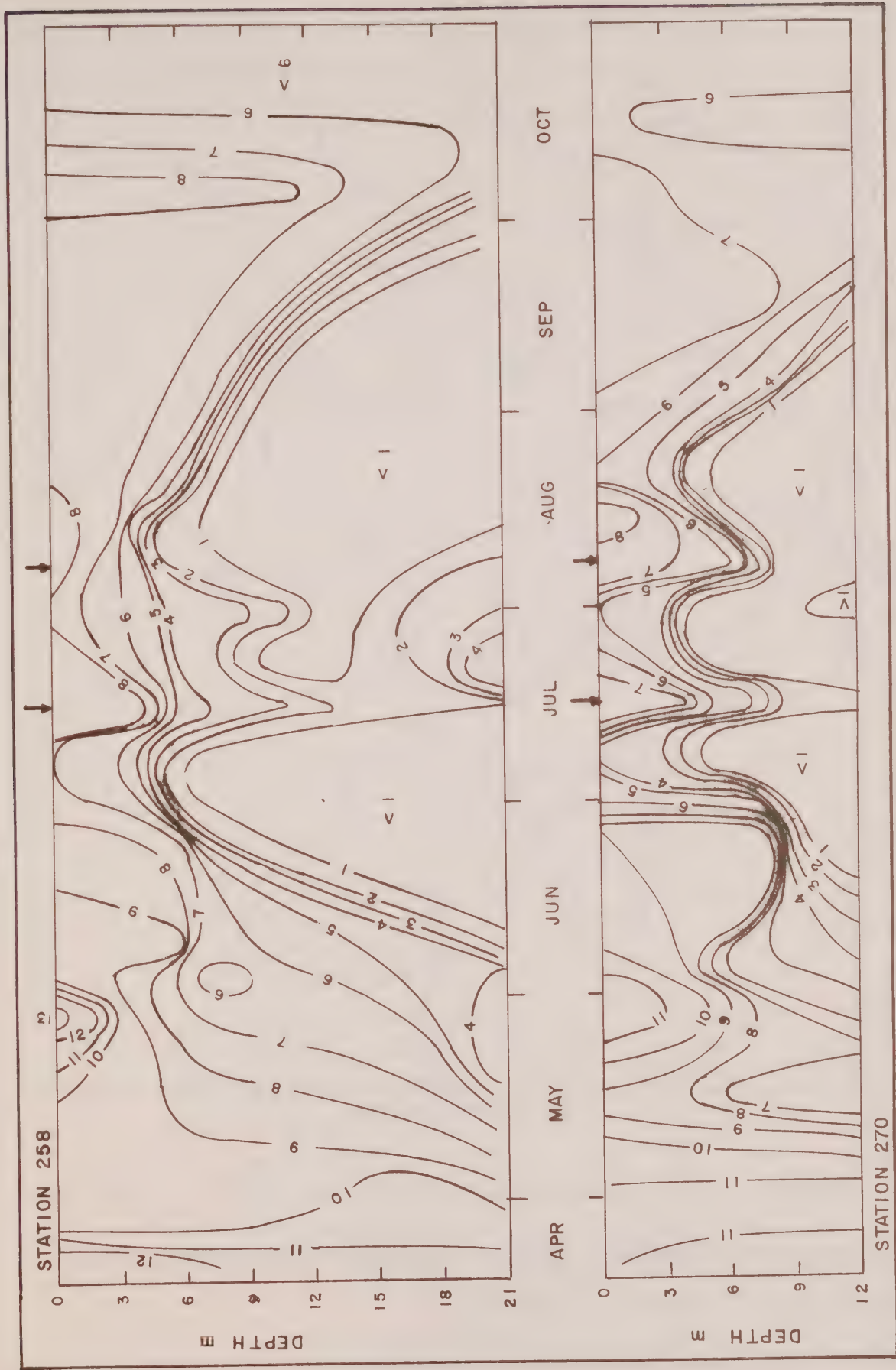


FIGURE 4 CONTINUED: DISSOLVED OXYGEN ISOPLETHS (1975)

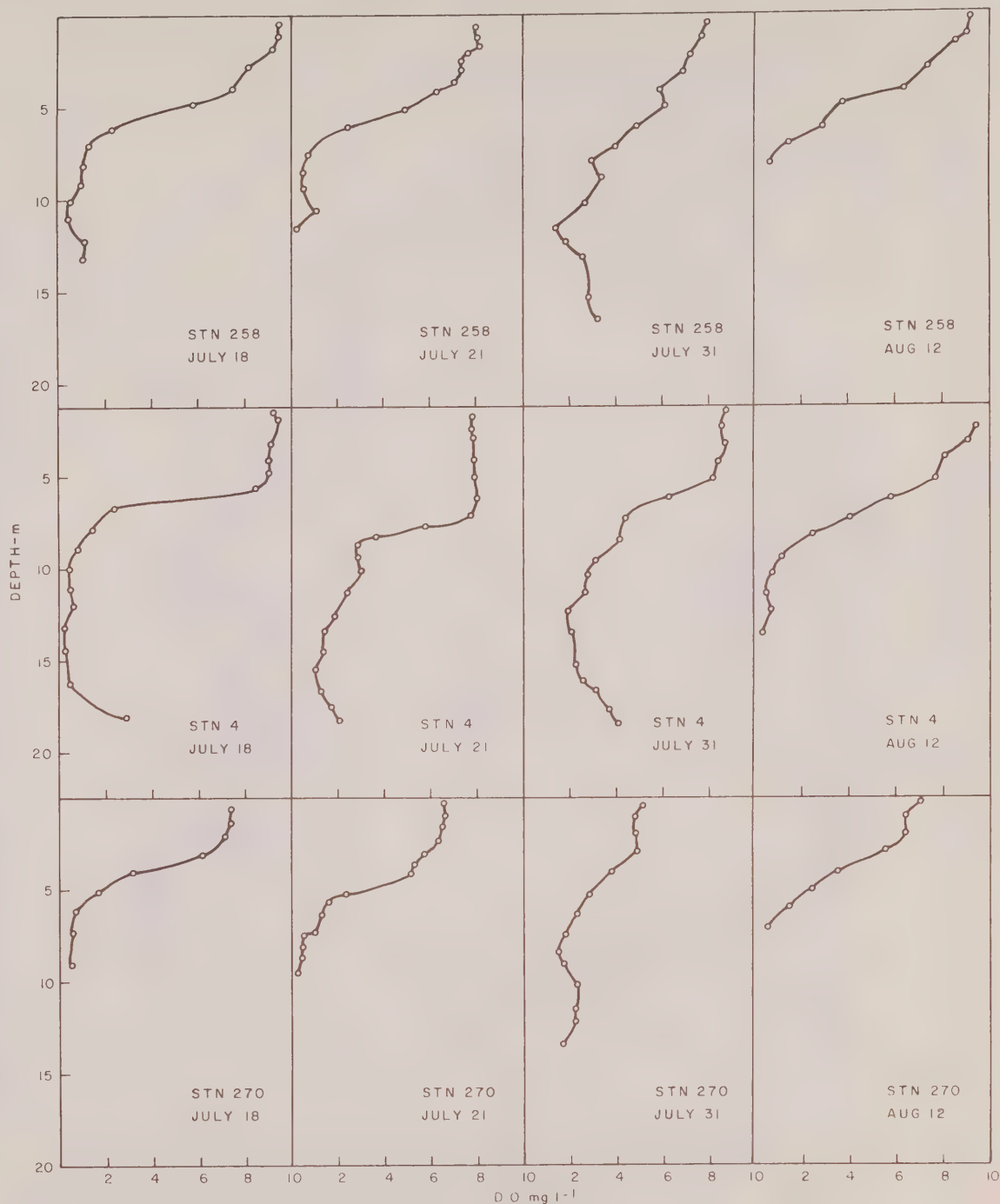


FIG. 5 DISSOLVED OXYGEN - DEPTH PROFILES DURING THE MIXING PERIOD. (mg/l). (1975)

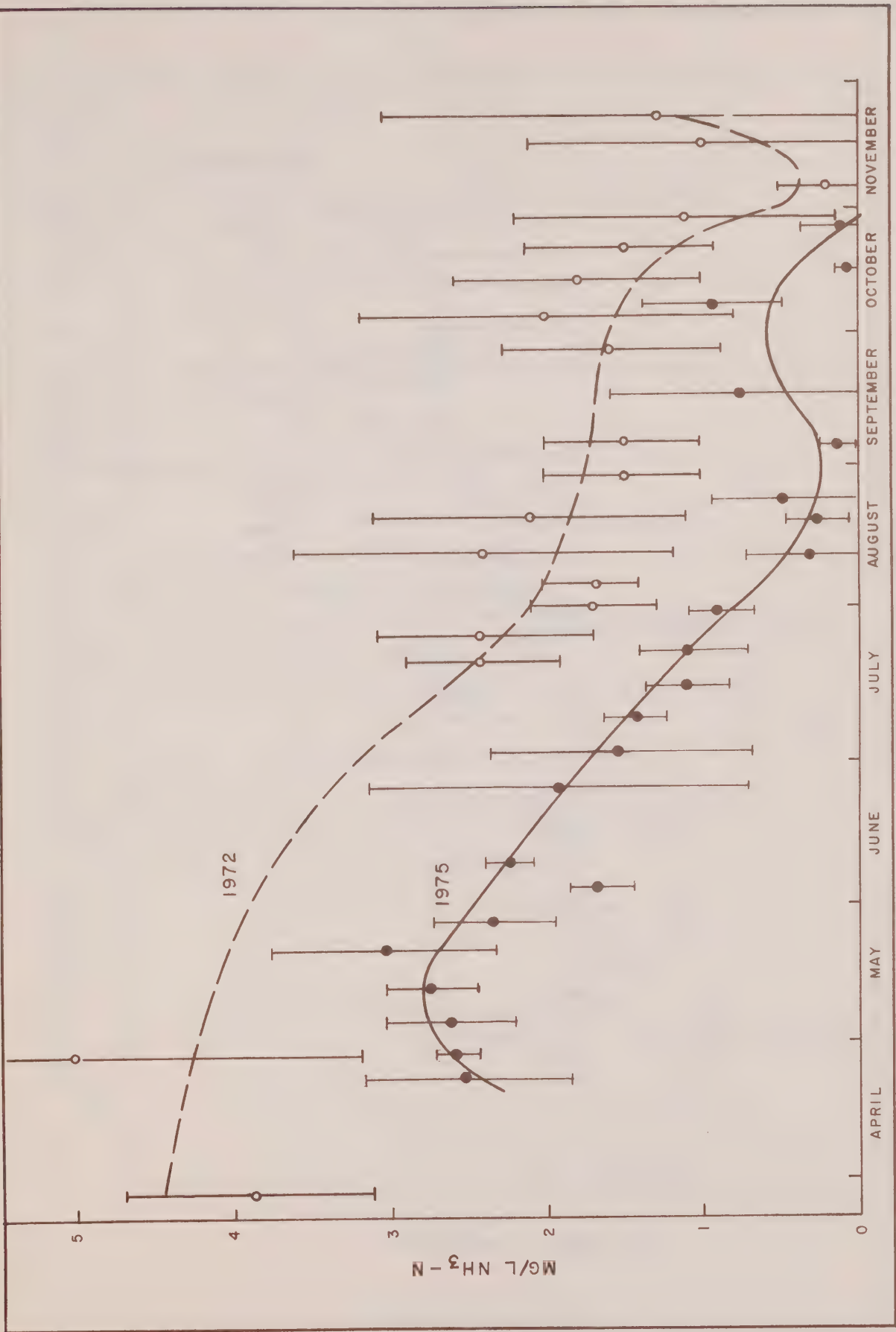


FIGURE 6: SEASONAL TRENDS OF AMMONIA IN 1972 AND 1975

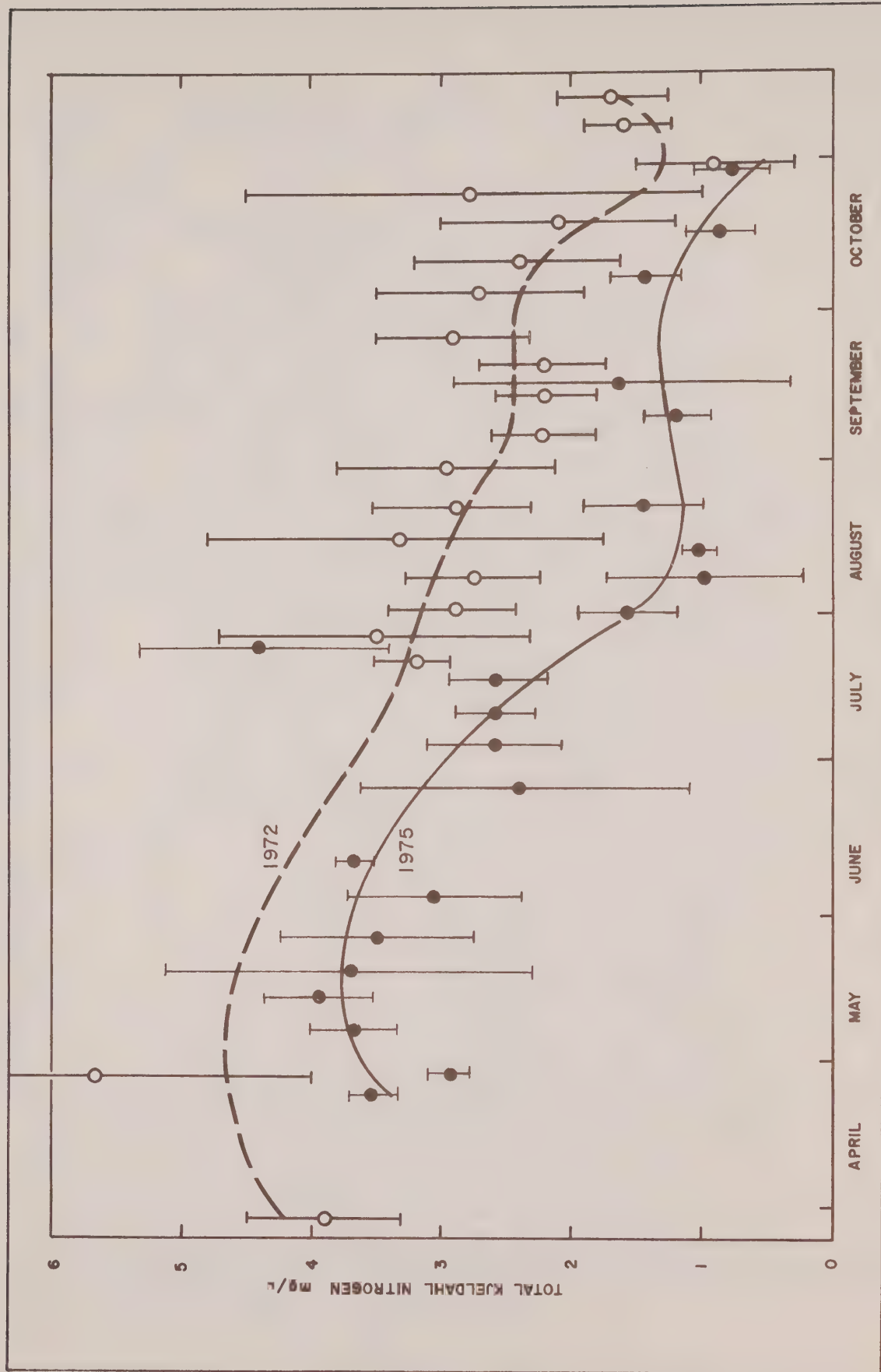


FIG. 7 SEASONAL TREND OF TOTAL KJELDAHL NITROGEN IN 1972 AND 1975



FIG. 8 TEMPORAL AND VERTICAL DISTRIBUTION OF NH_4 (mg/l). (1975)

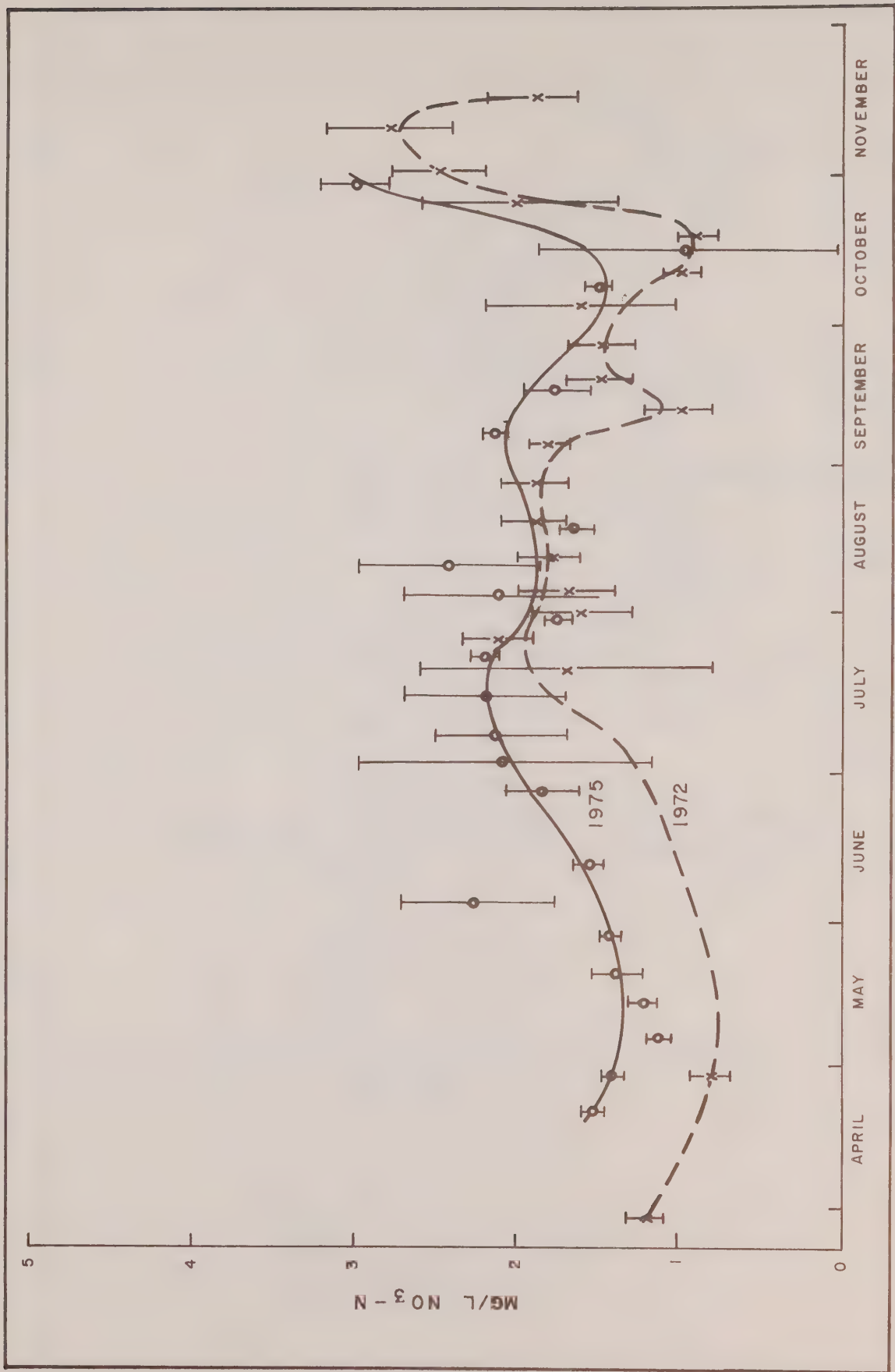


FIGURE 9 : SEASONAL TRENDS OF NITRATE IN 1972 AND 1975

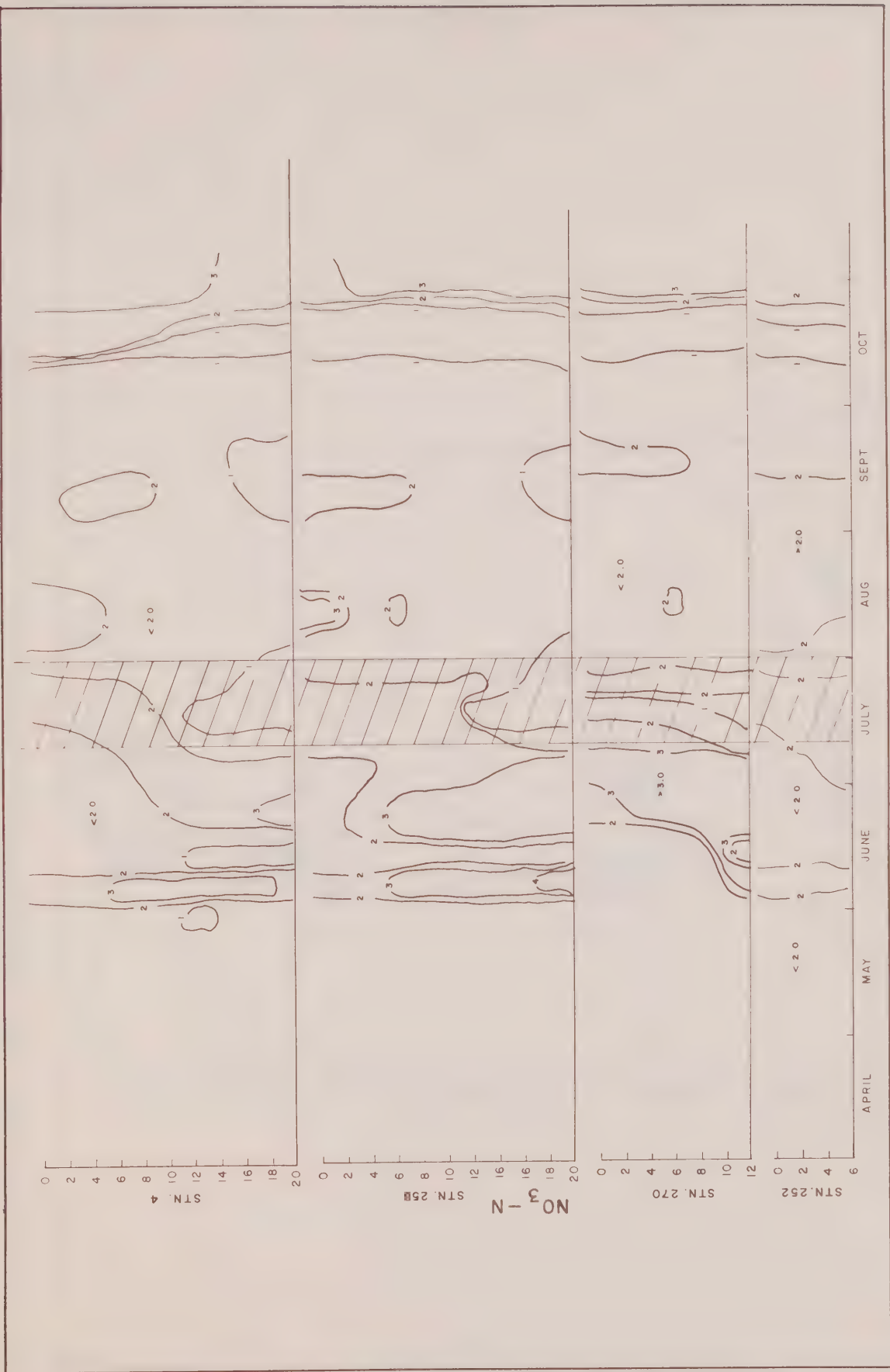


FIG. 10 VERTICAL AND TEMPORAL DISTRIBUTION OF NO_3^- (mg/l) AT STATIONS 4, 258, 270, AND 252. (1975)

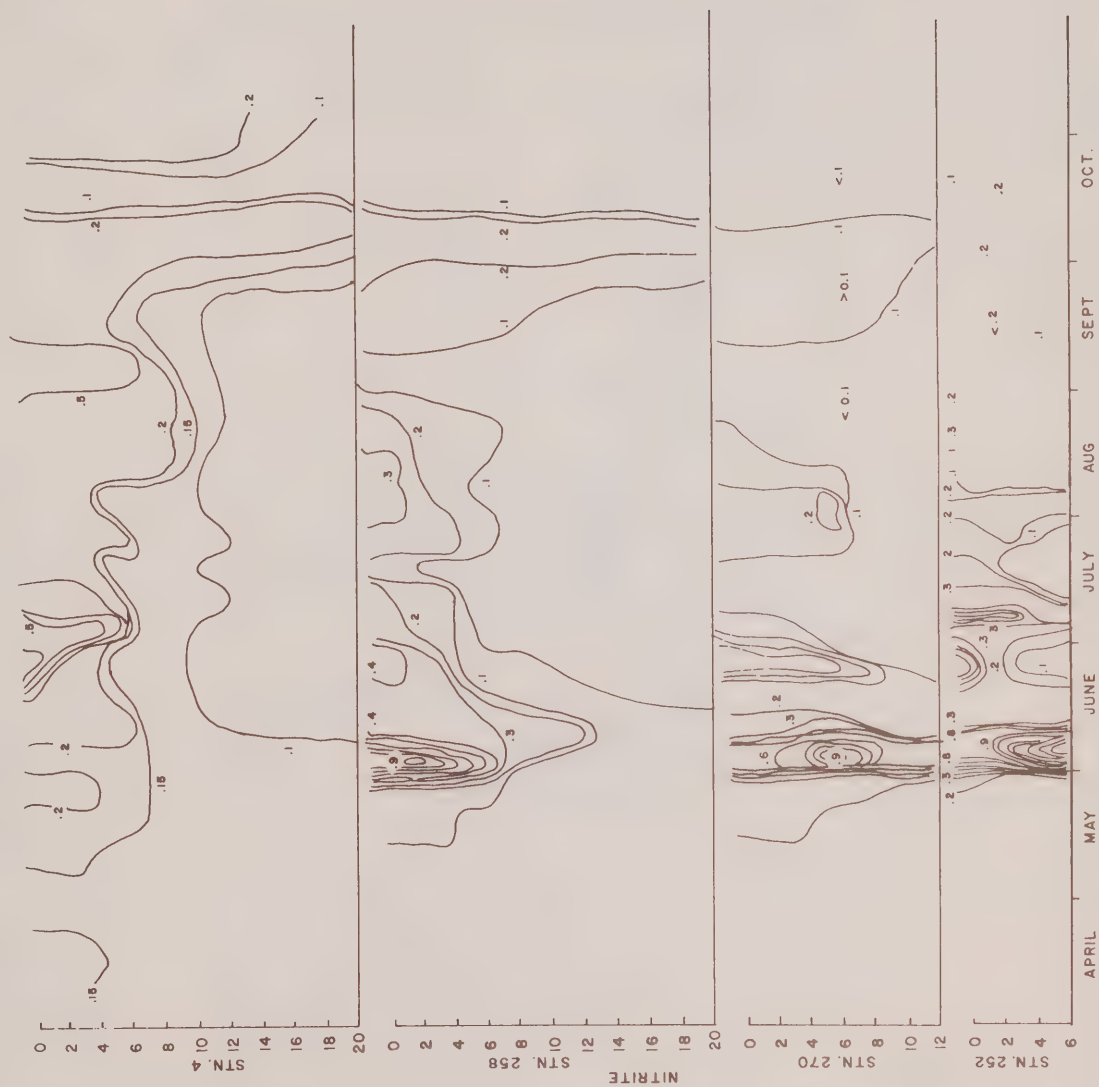


FIG.11 VERTICAL AND TEMPORAL DISTRIBUTION OF NITRITES (mg/l).



FIG. 12 VERTICAL AND TEMPORAL DISTRIBUTION OF SOLUBLE REACTIVE PHOSPHORUS ($\mu\text{g/l}$) (1975)

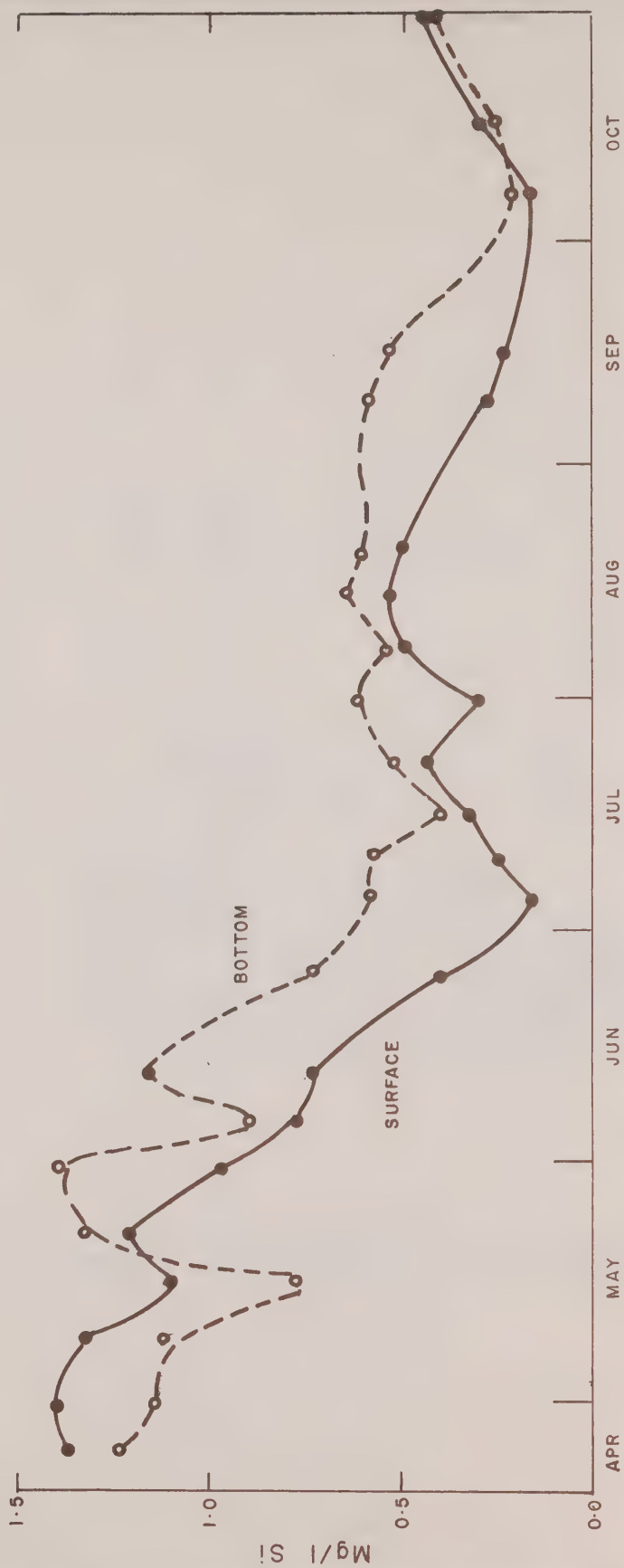


FIGURE 13: VARIATION OF SILICA WITH SAMPLING DATE, 1975 SURFACE AND BOTTOM MEANS

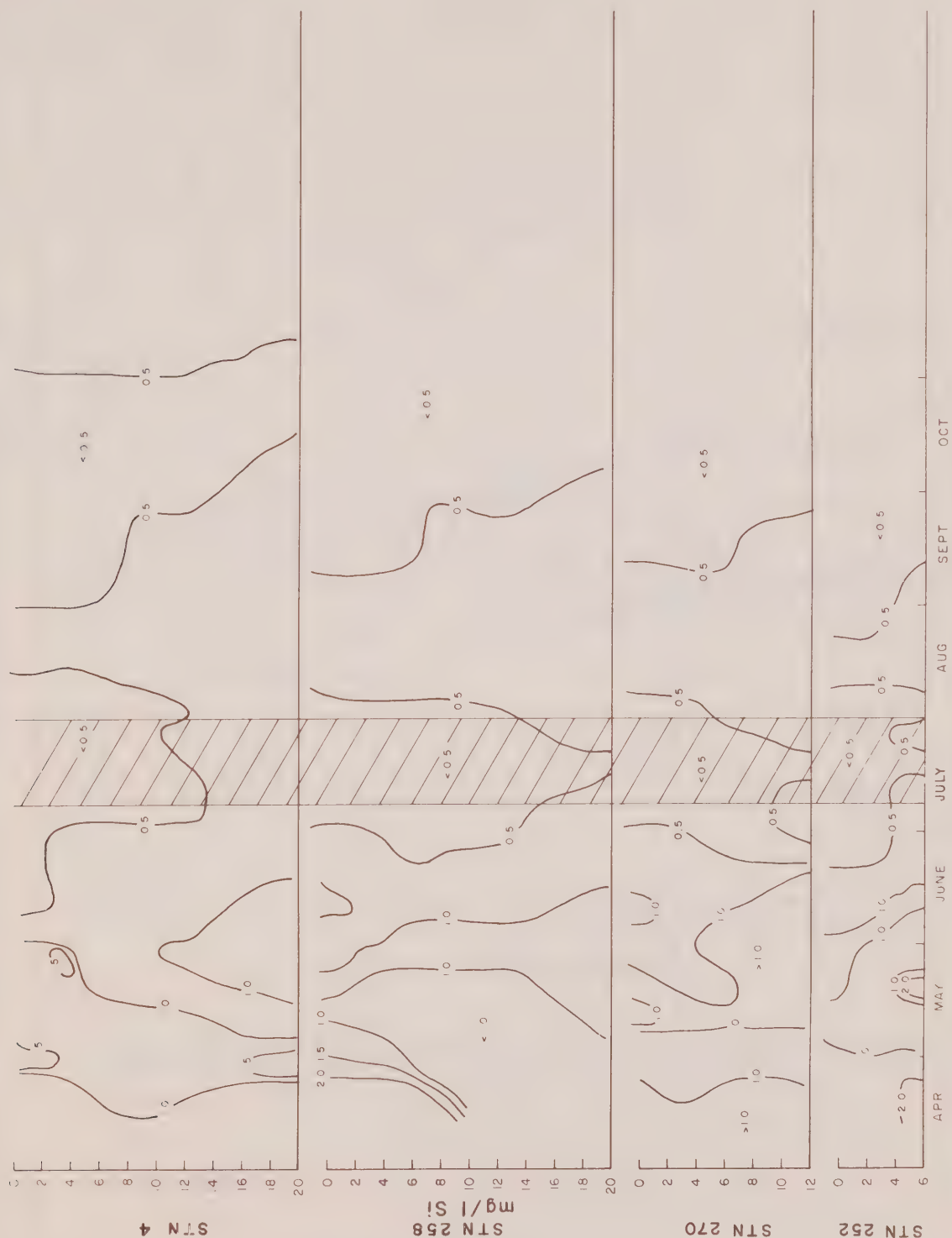


FIG.14 : VERTICAL AND TEMPORAL DISTRIBUTION OF DISSOLVED REACTIVE SILICATES (mg/l) AT STATIONS 4, 270, 258, 252, 1975.

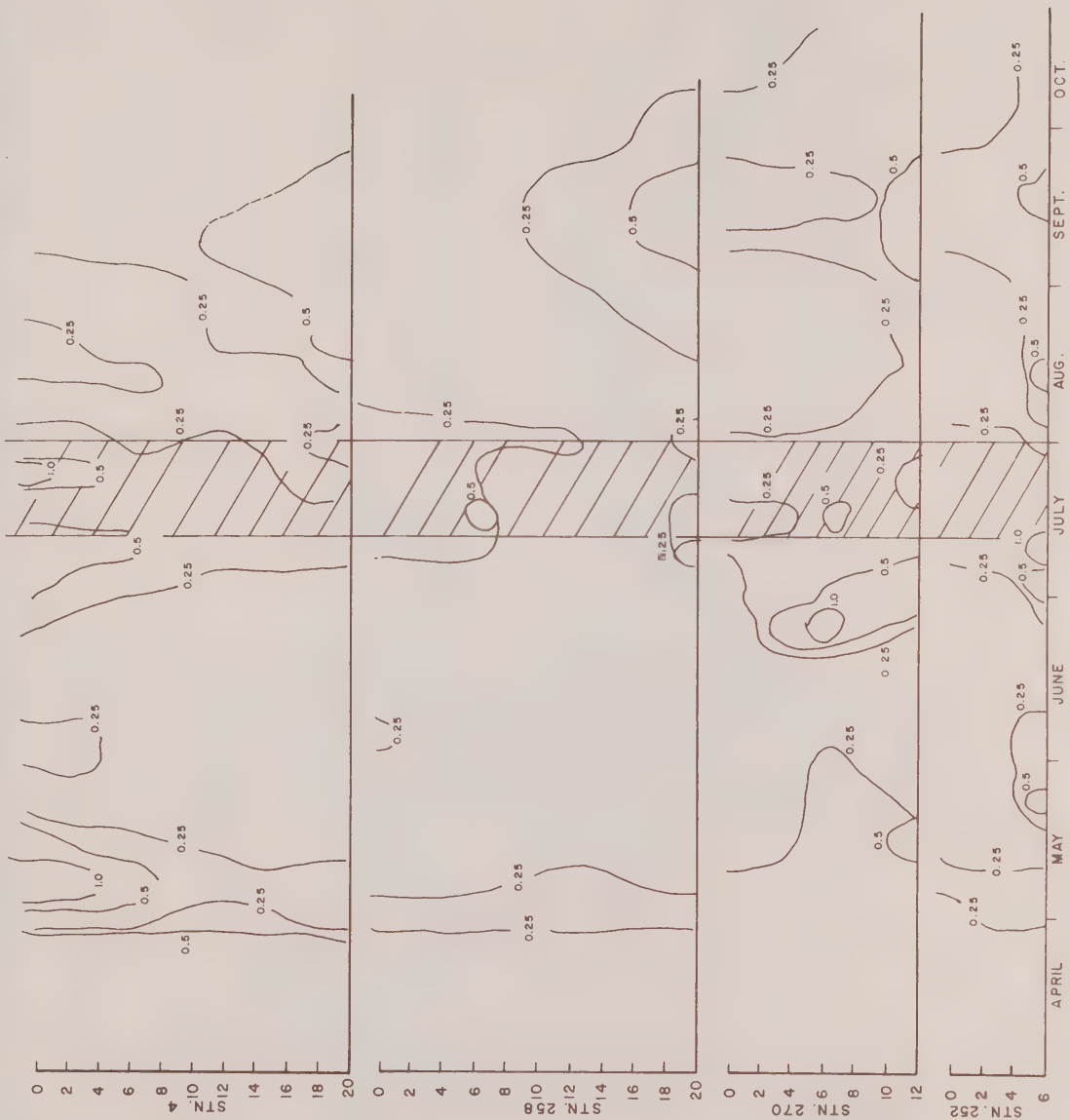


FIG. 15 VERTICAL AND TEMPORAL DISTRIBUTION OF IRON (mg/l) AT STATION 4, 258, 270, AND 252 1975

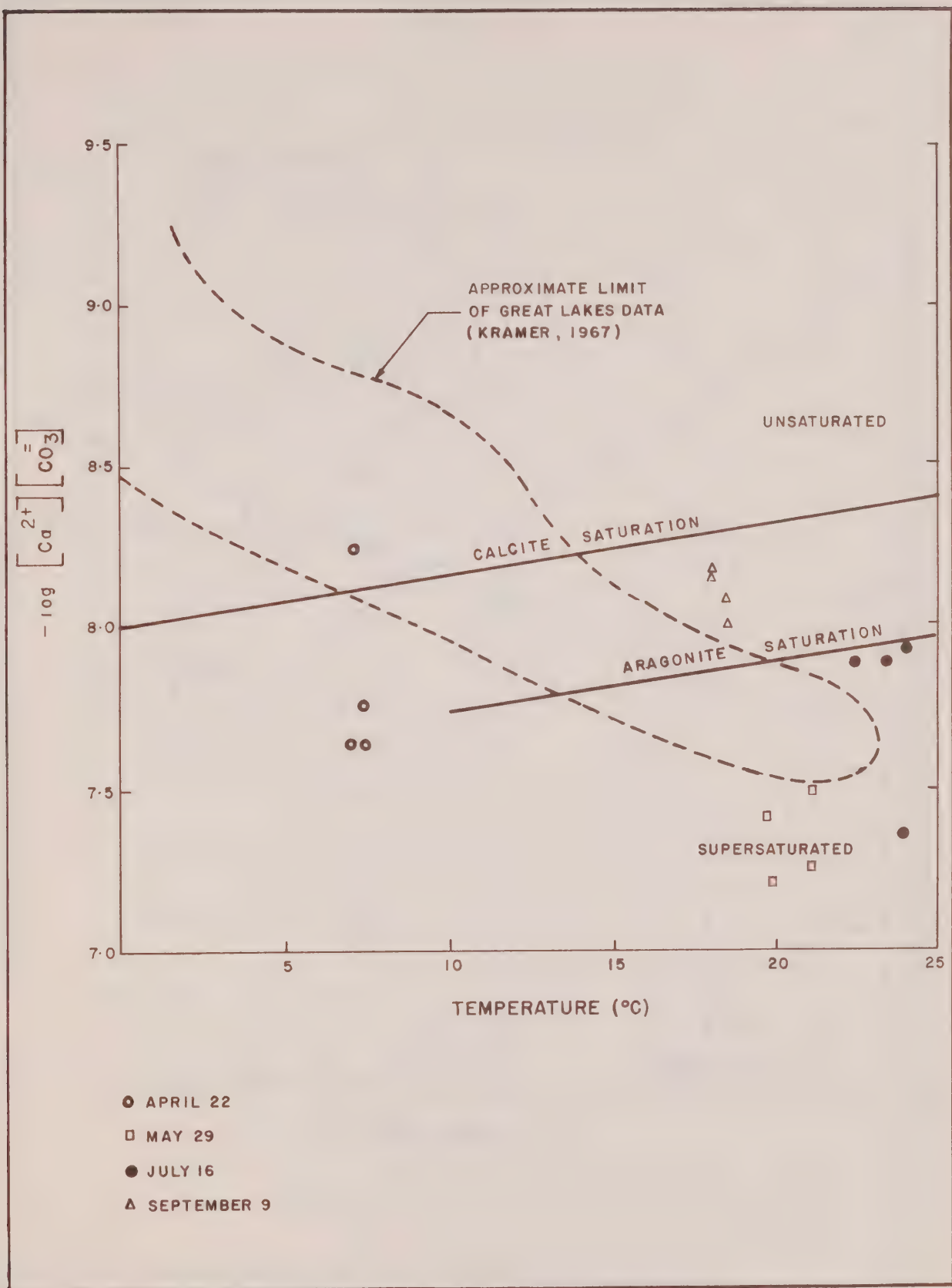


FIGURE 16: SATURATION OF HAMILTON HARBOUR AND GREAT LAKES WATER WITH RESPECT TO CALCITE (AFTER KRAMER, 1967)

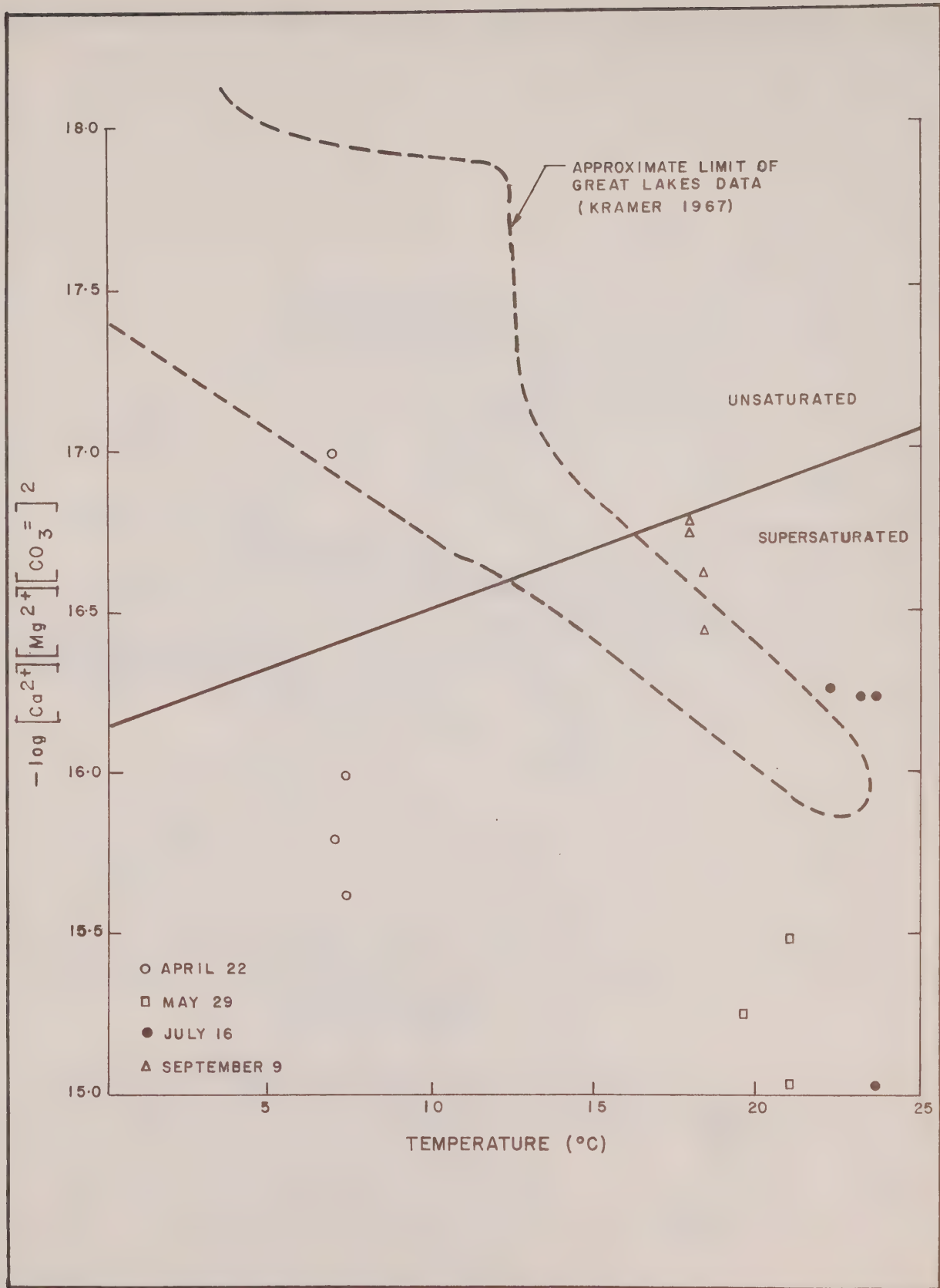
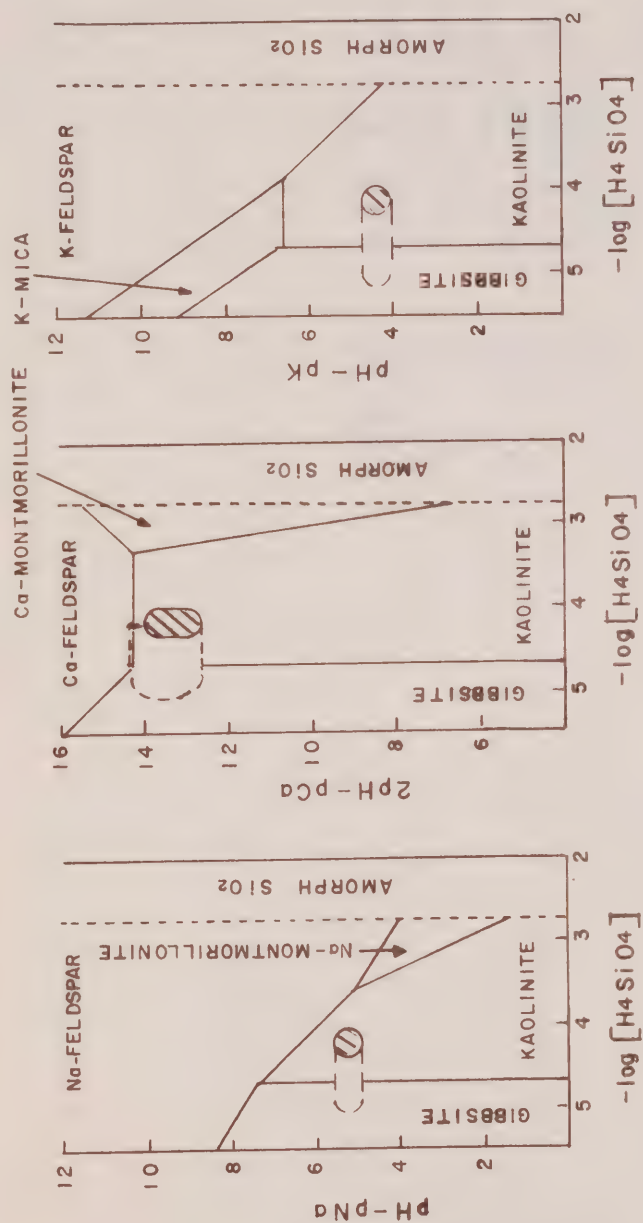


FIGURE 17: SATURATION OF HAMILTON HARBOUR AND GREAT LAKES WATERS WITH RESPECT TO DOLOMITE (AFTER KRAMER, 1967)



FIGURES FROM STUMM AND MORGAN 1970 Pg 404

◐ INDICATES RANGE OBSERVED IN APRIL, 1975

----- INDICATES RANGE OBSERVED IN SUMMER (MAY-SEP) DATA

FIGURE 18: EQUILIBRIA OF SILICATE MINERALS IN HAMILTON HARBOUR

HAMILTON HARBOUR STUDY '75

section B

Mixing

HAMILTON HARBOUR STUDY

SECTION B

ARTIFICIAL MIXING OF HAMILTON HARBOUR 1975

SUMMARY

HAMILTON HARBOUR ($79^{\circ}50'W$, $43^{\circ}17'N$) IS AN ENCLOSED BODY OF WATER CONNECTED TO THE WESTERN END OF LAKE ONTARIO VIA A SHIPS' CHANNEL. LAKE EXCHANGES OF THE ORDER OF 1 PERCENT OF THE HARBOUR VOLUME PER DAY, AND AVERAGE INTERNAL CURRENTS OF 3 CM SEC^{-1} PREVENT STABLE TEMPERATURE LAYERS OF WARM SURFACE WATERS AND COLD BOTTOM WATERS FROM FORMING. IF SUCH LAYERING IS ESTABLISHED, THE BOTTOM WATERS BECOME DEPLETED IN DISSOLVED OXYGEN. BECAUSE OF THE NATURAL INSTABILITY OF THESE STRATA, HOWEVER, EFFECTIVE ARTIFICIAL MIXING REQUIRES LITTLE ENERGY TO CIRCULATE THE HARBOUR WATERS. DURING 1975, ARTIFICIAL MIXING WAS SUFFICIENT TO WEAKEN THE STRATA TO THE EXTENT THAT DISSOLVED OXYGEN WAS RETURNED TO THE LOWER DEPTHS OF THE HARBOUR. THIS REAERATION WAS ACCOMPLISHED WITH AN AIR DIFFUSER BY LIFTING THE DENSE LOWER WATERS TO THE SURFACE WHERE ATMOSPHERIC AERATION INCREASED THE DISSOLVED OXYGEN CONTENT.

AN INTENSIVE SURVEY OF PRIMARY NUTRIENTS, HEAVY METALS, MINERAL CONTENT, PHYTOPLANKTON ABUNDANCE AND PRODUCTION, AND BACTERIAL POPULATIONS WAS PERFORMED. RELATIVE ABUNDANCE OF ZOOPLANKTON AND FISH POPULATIONS WAS DETERMINED. DURING THE LIMITED PERIOD OF MIXING (JULY-AUGUST, 1975) DISSOLVED OXYGEN INCREASED FROM NEAR 0 MGL^{-1} TO 2 MGL^{-1} THROUGHOUT THE LOWER WATER COLUMN. THERE WERE NO SIGNIFICANT CHANGES IN HEAVY METALS AND MINERAL CONTENTS, BUT TOTAL PHOSPHORUS CONCENTRATIONS BECAME MORE HOMOGENOUSLY DISTRIBUTED WITH DEPTH, DECREASING SURFACE CONCENTRATIONS. PHYTOPLANKTON PRODUCTION AND STANDING CROP INCREASED, AND BACTERIAL POPULATIONS DECLINED. ZOOPLANKTON INCREASED THEIR VERTICAL HABITAT BUT FISH, HOWEVER, BECAUSE OF THE LIMITED PERIOD OF MIXING DID NOT RESPOND. IT WAS APPARENT THAT ARTIFICIAL MIXING INCREASED THE WASTE ASSIMILATION POTENTIAL OF THE HARBOUR,

HAMILTON HARBOUR ARTIFICIAL MIXING REPORT

Recent studies by the Ontario Ministry of the Environment have indicated that hypolimnetic anoxia is a critical factor influencing the water quality of Hamilton Harbour. In the first Hamilton Harbour Report (MOE 1974) artificial mixing was suggested as a possible method to assuage hypolimnetic anoxia. A review of artificial mixing presented in the second study report (MOE 1975) indicated that responses to artificial mixing were varied. A survey by the American Water Works Association (1970) indicated the 90% of mixing trials were considered successful with respect to improved water quality and biological production. Because of the complexity of the physical-chemical-biological interactions in Hamilton Harbour and varied responses to artificial mixing, it was not possible to predict the effects of vertical circulation of the harbour waters.

Hamilton Harbour is an unique body of water. It is a natural harbour, sheltered from Lake Ontario by a narrow sandbar. The harbour has a volume of $2.8 \times 10^8 \text{ m}^3$ and mean depth of 13 m. Industrial water use is estimated to be $27 \text{ m}^3 \text{ sec}^{-1}$, with waste waters returned into the harbour. Treated urban wastes enter the harbour directly at a rate of $3.2 \text{ m}^3 \text{ sec}^{-1}$ with an additional annual loading of $0.1 \text{ m}^3 \text{ sec}^{-1}$ from storm sewers during overflow periods. Nitrogen loading was determined to be five times the harbour stock, and phosphorus loading was thirty times higher than the calculated harbour stock. Much of the nutrient loading was into the epilimnion of the harbour, and artificial mixing was suggested as a means to reduce epilimnetic concentrations and increase the capacity of the harbour to assimilate these high effluent loadings by providing a suitable environment for aerobic decomposition.

The primary effects of artificial mixing are basically dependent on the total energy used for mixing and the efficiency of the transfer of this energy to the water mass. As stratification is a cumulative process, the energy input required for destratification must be greater than the rate at which the energy of thermal stabilization is increasing. If the input of the mixing system and natural turbulence is equal to or is less than the energy of stratification, the rate of increasing thermal stabilization will be zero or correspondingly reduced. In this respect the terms artificial mixing and destratification are not synonymous. Most mixing attempts are designed to destratify the water column, although systems have been designed which can prevent stratification or maintain a certain degree of thermal stabilization.

It is possible that chemical reactions, as described by Stumm and Morgan (1970), can be predicted within a body of water. Most of these reactions are either adsorption and precipitation, complexation, oxidation and reduction, acid-base reactions, and biotic absorption and assimilation. It is the last component which places the artificial mixing of Hamilton Harbour or any body of water into the realm of being experimental design. Chemical and physical responses could be predicted from basic thermodynamic relationships, if these parameters were not interrelated with the biota of the harbour.

During periods of stratification, Hamilton Harbour is characterized by a number of horizontal isodensity strata. Perturbations between the strata are primarily induced by wind mixing and exchange via the ship channel (MOE, 1975). The theoretical effects of diffused air injection were described by Fast (1968). Basically, cold hypolimnetic waters are brought to the surface as a result of decreased density and entrainment with the bubbles from the diffuser. At the surface the upflow of water diverges and begins to sink below the warm epilimnetic waters. This downwelling is modified by the density strata, and at all times mixing occurs between the upwelled water and epilimnetic waters, forming new density strata. Koberg and Ford (1965) have noted that the rate of destratification decreases as a lake approaches isothermal conditions.

The review of artificial mixing in the Hamilton Harbour Report 1975 noted that unsuccessful attempts to relieve hypolimnetic anoxia are often the result of a poorly established oxidized microzone at the sediment-water interface. This would suggest that the sediment oxygen demand (both chemical and biological) might well be the driving force of oxygen depletion in the harbour, and oxygen demand within the water column to be a secondary factor. In Section E of the report it was found that oxygen uptake rates of $0.05 \text{ grams of oxygen m}^{-2} \text{ hr}^{-1}$ were sufficient to deplete the total oxygen stocks of the harbour, were it not for photosynthetic sources and mass exchange by the ship canal. It must be noted that photosynthesis is probably of little value to the oxygen budget as net oxygen production (photosynthesis minus respiration) could be low in the optically deep waters. Owens (1969) estimated that 69 percent of the oxygen content in the Thames estuary was derived from atmospheric reaeration, and only 8 percent from photosynthetic sources.

Within the water column artificial mixing can result in rapid oxidation and utilization of dissolved organic carbon. There are few studies on the effects of artificial mixing on the nature of the sediments. Fast et al (1972) found that

sediments were gelatinous and adhesive before aeration, and became loose after aeration as a result of a change from anaerobic to aerobic decomposers. Mercier (1955) was reported by Toetz et al (1972), to have stated that sediment thickness of Lake Brett was decreased as a result of maintaining an aerobic microzone over a period of years. This would suggest that organic sediment oxygen demands can be alleviated by artificial mixing, and in this aspect mixing can be considered as a corrective process. Hamilton Harbour receives the effluents of three sewage treatment plants (the Dundas plant via Cootes Paradise, the Burlington Skyway plant and the Hamilton Plant). It is probable that much of the organic nature of the sediments predates the Hamilton STP when raw sewage was discharged directly into the harbour. The sediments are high in organics as noted by loss on ignition data as high as 18 percent of the sediment content.

In general terms, artificial mixing, be it in a form of destratification or induced vertical mixing, increases the assimilation capacity of a body of water by creating 'sinks' (such as the loss of carbon dioxide, hydrogen sulphide, and ammonia to the atmosphere, and the loss of metals such as iron, manganese and aluminium to the sediments). It is not known just how efficient these processes are as many of these losses can be balanced by changes in chemical turnover rates, biotic adaptations and modifications of the thermodynamic equilibria of physical-chemical parameters.

Biological responses can dictate the success of artificial mixing when considering water quality whether it be for recreational purposes (Hooper et al, 1953) or for water supply (Ridley 1970, Steel 1972). Vertical circulation of a water column can change temperature regimes, light penetration and nutrient availability in a body of water. Empirical predictive models of phytoplankton responses have been developed, (Lorenzen and Mitchell, 1975), but these do not account for the large variations and responses outlined in the literature.

The effects of artificial mixing are not only palliative, and the success of artificial mixing must be based on an overview of the problem. Hamilton Harbour represents a very difficult ecological situation. The heavy input of nutrients, organics and thermal effluents combined with land filling operations have all contributed to the low water quality. In Hamilton Harbour artificial mixing is a treatment of the symptoms of eutrophication. To be considered successful, the mixing project must prevent hypolimnetic anoxia. Although not a corrective process, increased assimilation capacity and improved biological activity resultant from artificial mixing might reduce the deleterious effects of nutrient and waste loadings on water quality.

THE MIXING SYSTEM

Four diffuser lines were used to induce artificial mixing in Hamilton Harbour. The aerator lines were placed 61 m (200 ft) apart extending from the west wall of Stelco docks. Each line consisted of 5.08 cm (2 in) polyethylene tubing (80 psi working pressure). Three of the lines consisted of a 191 m (625 ft) delivery section attached to a 305 m (1000 ft) perforated line. The fourth line consisted of a similar delivery line with a 122 m (400 ft) perforated line. A 137 m (450 ft) steel header pipe connected the lines to a $0.28 \text{ m}^3 \text{ sec}^{-1}$ (600 cfm) compressor which was used to supply the aerator lines (Fig. 1).

Perforations were made in the diffuser section using a punch tool of 2 mm length and 0.35 mm width. Each 305 m (1000 ft) of aerator line contained 1465 slits. Starting from the far end of the diffuser, the slits were arranged as below:

- 1st 400 slits at 10.2 cm (4 in) intervals
- 2nd 600 slits at 20.3 cm (8 in) intervals
- 3rd 465 slits at 30.3 cm (12 in) intervals

This spacing was computed to obtain an even distribution of air flowing through each metre of diffuser at the operating air pressures. The diffuser line was kept approximately half a metre off the bottom, and was anchored at 4.5 m (15 ft) intervals by attached cement blocks.

Water pressure at a depth of 24.4 m (80 ft) of water is approximately 2.31 atmospheres (34 psi), and combined with losses to the line of approximately 1.02 atmos (15 psi), there is an internal design pressure of approximately 3.4 atmos (50 psi). As the compressors should be operated at under 5.4 atmospheres to prevent oil in the line, the pressure available at each aperture is 0 to 2.0 atmos (0 to 30 psi). Extensive tests at the Ontario Hydro Hydraulics Laboratories suggested that the mean flow at each aperture would be between $23\text{--}39 \text{ cm}^3 \text{ sec}^{-1}$ (35 cfh) at 0.8 atmospheres (12 psi) assuming $0.047 \text{ cm/sec}^{-1}$ (100 cfm) at atmospheric pressure from the compressor to each line.

Figure 2 is a schematic representation of the dates of installation of the four aerator lines. The lines were numbered consecutively from the north most position. The operation of the diffusers was affected by shipping in the docking area which severed the lines on several occasions. Only towards the end of July 1975 were all lines operating effectively with a $0.17 \text{ m}^3 \text{ sec}^{-1}$ (350 cfm) total flow. At this rate of flow assuming an entrainment factor of 10, it would take approximately 700 days to mix the epilimnetic and hypolimnetic volumes of the harbour at this time of year.

On its own the mixing system is inadequate but other physical factors; such as higher entrainment factors, advective flow, exchange periodicities at the thermocline and wind stress modify the physical behavior of the water mass, producing less stable water masses than would be expected. In shallow parts of the harbour (less than 10 meters) these factors alone could produce several complete destratifications each year. These destratifications are periodic and are related to the geometry of the harbour and periodicities of Lake Ontario. In many circumstances the extra work required to maintain isothermal conditions is only 3-4% of the surface wind work (Steel, 1972); provided some mechanism exists for transforming shear through the thermocline. The alteration of the isodensity strata would be such a mechanism to induce greater wind work which generates currents and increases the advective processes in the water body.

THE RESULTS OF ARTIFICIAL MIXING

a. Temperature and Dissolved Oxygen

The primary effect of artificial mixing is the modification of the density strata within the body of water. The usual sequence of events would be the lowering of the thermocline. The time required to lower the thermocline until achieving isothermy, depends on factors such as volume, stability of stratification, intensity of solar radiation, wind effects etc. Generally, there is a surface cooling effect and an increase in the temperature of the hypolimnetic waters. Surface cooling was evident in Hamilton Harbour, as the surface temperatures dropped from 26°C to 22°C (Fig. 3). Although there was an atmospheric disturbance on July 25, (Fig. 2) it is doubtful if this drop in mean air temperature could result in such cooling effects. An intrusion of warm epilimnetic water into the hypolimnion was noted in July, but this was probably related to natural mixing. The lack of any good indication of an increase in hypolimnetic temperatures (increased 4°C) was a result of the shallow depth of the epilimnion (~ 6 m) as compared to the hypolimnion (~ 14 m). It is apparent that the shallow stations 270 and 252, of 12 meters and 6 meters depth respectively, do not form stabilized water columns. Only the deep basins (as demonstrated at stations 258 and 4) have density strata which are somewhat stabilized. Station 4 has the highest temperatures within the water column as it receives the warm effluent of the Windermere Basin.

The artificial mixing of Hamilton Harbour, during the period of July to August 16, did not result in any major changes in the thermal structure. As the water column of the harbour is naturally unstable (MOE, 1975), it was difficult to determine which changes were related to the mixing experiment.

In Figure 2 (mean wind and air temperatures), it is noted there is no evidence of atmospheric changes such as high winds or substantially low temperatures to account for modifications in the thermal profile. Thus, artificial mixing probably accounted for the modest alteration of the iso-density strata.

One of primary objects of artificial mixing is aeration. The efficiency of aeration depends on the oxygen tensions existing in the water (Roeber et al, 1965). It is not known if the diffuser was a significant source of oxygen, but without doubt surface exchange dominated the aeration aspect of artificial mixing of Hamilton Harbour. The pumping rate was small compared to the harbour volume. Even if 20% of the oxygen was absorbed by the water, less than 0.1 mg l^{-1} of oxygen would be added to the harbour after one week of aerating at a rate of $0.17 \text{ m}^3 \text{ sec}^{-1}$ (350 cfm).

The dissolved oxygen content of Hamilton Harbour increased during vertical circulation of the harbour waters. On July 18 with two diffuser lines operating there is a well defined anoxic hypolimnion (Fig. 4). There is a slight increase in dissolved oxygen content at the bottom of Station 4 perhaps as a result of influences of Lake Ontario water. On July 21 there was a marginal improvement of station 4, as the hypolimnetic oxygen concentration increased to 1.0 mg l^{-1} . On July 31, however, with four diffuser lines operating all stations had measurable dissolved oxygen concentrations (greater than 1 mg l^{-1} throughout the water column). During the first week of August only two diffuser lines were operating (lines 1 and 4) and anoxic conditions returned. Frequent damage by ships to the aerator left only one line functional by August 16. On August 19, the one remaining line failed. After being repaired and repositioned, line 1 operated from August 22 to the end of September with little effect on the dissolved oxygen content. From these observations, it was demonstrated that a flow of air in excess of $0.14 \text{ m}^3 \text{ sec}^{-1}$ (300 cfm) was required to have a beneficial effect on the hypolimnetic anoxia. Because of the short period of operation of the four lines, there was little measurable improvement in the overall standing stock of dissolved oxygen. Considering the warm summer compared to previous years, the beneficial effects of artificial mixing would probably be disguised by increased oxygen demand. It must be noted that artificial mixing was successful in increasing the dissolved oxygen content of the harbour in a very short period of time. Continuous vertical circulation could be expected to restore the dissolved oxygen to the extent that the fish and zooplankton habitats would be extended to greater depths.

Changes in the dissolved oxygen content of Hamilton Harbour have been related to lake water incursion through the ship canal. To resolve whether the increase in the dissolved oxygen content of the harbour was related to lake water incursions or artificial mixing, redox potential was used to differentiate the two water masses. Figure 5 illustrates the redox potential at three stations during the mixing period. Redox potentials are difficult to interpret, but in general, can be expected to be in the range of 400-500 mv for oligotrophic lakes such as Lake Ontario with the actual value being dependent on the oxygen-hydroxyl system as outlined below:



$$\text{Eh} = 1.234 - (0.058 \text{ pH}) - (0.0145 \log \text{Po})$$

where Po is the partial pressure of oxygen.

In Hamilton Harbour, the Eh values measured are about 200 mv and clinograde Eh curves occur suggesting little influence of Lake Ontario at the sampling stations. Hutchinson (1957) indicated that low Eh, with clinograde distributions, was dependent on other redox systems. The redox potentials of Hamilton Harbour might well be dependent on the Fe^{++} - Fe^{+++} and nitrate-ammonia systems with the presence of sulphide and/or dissolved organic material resulting in further complications. It is possible that the Eh of the waters would have to be raised to a critical level before the dissolved oxygen concentration would increase. Artificial mixing resulted in orthograde Eh profiles (See Fig.5). Under conditions of orthograde Eh, the absolute value of Eh is important at the sediment-water interface as it influences the solubility of nutrients in the sediment. It is by this parameter that the establishment of an oxidized microzone at the interface can be determined.

B. Responses of Nutrients and Heavy Metals

The distribution of non-conservative parameters often reveal varying degrees of over-dispersion (variance > mean). Departure from Poisson distributions can either be positive or negative. As a result of sedimentation, current and turbulence patterns resulting in non-equal mixing, effluent outfalls and shoreline effects; over-dispersion is frequently encountered in aquatic habitats. When trying to statistically assess significant relationships between any parameter and artificial mixing, it is extremely difficult to determine if a change in concentration or distribution of a certain parameter is related to artificial mixing. In the following discussion there has been no attempt to statistically relate the chemical or physical changes to artificial mixing. Chemistry and statistical trends will be more fully discussed in Section A.

All metals were monitored as depth composites at stations 252, 4, 270 and 258 at regular time intervals during 1975. Lead and molybdenum, cadmium, copper, chromium, manganese, cobalt and nickel concentrations did not illustrate any definite response to artificial mixing. Zinc increased during the mixing period, but this might be a result of increased atmospheric loading into Hamilton Harbour, however, no data were available in 1975. Shiomi and Kuntz (1973) found that atmospheric loading was a significant source of zinc in Lake Ontario. Chloride, sulphate, magnesium, calcium, potassium and sodium were not monitored intensively enough to note any effects of artificial mixing. It was noted by Haynes (1973) that calcium, magnesium, potassium and chloride were not affected during the artificial mixing of Kezar Lake. It must be noted, however, that calcium can have varied responses (Fast 1971, Symons, Irwin and Robeck 1968).

The distribution of iron is outlined in Figure 6. It is often reported in the literature that iron and manganese concentrations decreased during periods of mixing (Symons, Carswell and Robeck, 1969; Wirth and Dunst 1967). The decreases are usually related to the moderately soluble Fe^{++} being oxidized to the relatively insoluble Fe^{+++} . In Hamilton Harbour there was no evidence of a decline in total iron concentrations. Similar results were found by Lackey (1972) who noted that levels of iron and manganese did not change substantially in an artificially mixed lake. As a result of high iron loadings into the harbour and the relatively short period of mixing, it is reasonable to assume that changes in iron concentrations would not be expected.

In some circumstances, induced vertical mixing can result in definite responses by nutrients associated with phytoplankton production (Haynes, 1973). Although the components of the mineral contents of the water are necessary for phytoplankton production, the biogeochemical cycling of these elements is not directly related to these organisms, and concentrations are seldom, if ever, limiting. The different responses of calcium, however, might be a result of precipitation when autotrophs assimilate CO_2 from the system.

Elements related to biological processes often assume unpredictable distribution as a result of artificial destratification. This is particularly true of phosphorus. As phosphorus has high turnover rates, it is difficult to determine nutrient limitations by measuring the standing quantity of phosphorus. Changes in concentration are not simply related to algal production, as precipitation, adsorption and redox reactions occur. It is necessary to have mass balance budgets before a response to artificial mixing can be quantified. Most reports on the effects of artificial

mixing on phosphorus relate to changes of distribution (Hooper et al 1953, Leach and Harlin 1970) and not to changes in concentration (Bernhardt and Hotter 1967; Hyanes 1971).

There were no distinct trends in the total phosphorus or soluble phosphorus during the period of induced vertical mixing in Hamilton Harbour. In Figure 7a soluble phosphorus appears to have a high degree of temporal and spatial contagion. It is difficult to relate this distribution to biological activity, but it was noted that the periods of minimum soluble phosphorus were associated with high bacterial activity on June 4 and high phytoplankton standing crops on July 16. In general, however, there appears to be no strict relationship between changes in phosphorus concentration and distribution are more related to precipitation or changes in loading rates.

Figure 7b illustrates the vertical profiles to total and soluble reactive phosphorus at Station 258. Before diffused air was injected at a rate of $0.14 \text{ m}^3 \text{ sec}^{-1}$ (300 cfm) epilimnetic concentrations of total phosphorus exceeded hypolimnetic concentrations. On July 31 epilimnetic concentrations were comparable to hypolimnetic concentrations. As the vertical profile of chlorophyll *a* (Figure 15b) does not correspond, it would appear as if the modification of the total phosphorus profile is not simply related to the redistribution of the phytoplankton.

Dissolved silica levels are often stratified in natural lakes as a result of the wax and wane of diatom populations. This is well represented in Figure 8 which reveals decreasing concentrations of silica during the spring diatom growth, resulting in low concentrations in the epilimnion and higher concentrations in the hypolimnion.

As silicates do not depend on a reduced environment to become soluble (Cheng and Tyler, 1973), there were no definite responses to artificial mixing. During the period of July 16 to July 23 silicates were evenly distributed with depth. This might well be related to artificial mixing, but it is quite likely that other physical parameters were operating.

The nitrogen cycle of Hamilton Harbour is strongly dependent on biological activity. Changes in the ratio of $\text{NO}_3:\text{NO}_2:\text{NH}_3$ reflect the composition and activity of the bacterial flora of the harbour as well as industrial loading. This is particularly true during the winter period as ammonia concentrations increase as a result of industrial loadings and the low activity of the nitrifiers (Figure 9). From the

spring to the autumn there is a decrease in ammonia perhaps as result of increased activity of nitrifiers and some direct uptake of ammonia by the phytoplankton.

Nitrate values were slightly higher in 1975 than in 1972. Before hypolimnetic anoxia was developed (June 4), nitrate concentrations were greater in the hypolimnion than in the epilimnion, probably as a result of phytoplankton assimilation in the upper density strata. Once anoxia was developed, however, nitrates were reduced as denitrification rates increased. Figure 10 illustrates that during the mixing period there was no associated response by nitrates. Sustained artificial mixing might well have favoured nitrification processes, representing a positive response of the harbour to artificial mixing. The nitrogen system is suspected as being an important contributor to the low Eh. A shift towards nitrate would represent a positive response of the harbour to artificial mixing.

Nitrite is a relatively unstable intermediate in the nitrate-ammonia system. Although it is usually recorded in low concentrations, nitrite accumulates in Hamilton Harbour and reached concentrations of 1.85 mg l^{-1} . This chemical environment is reflected by the low Eh measurements. The activity of facultative anaerobic bacteria can have a profound effect on the behaviour of the nitrogen species. Paine and Riley (1969) felt that nitrates suppressed the reduction of $\text{NO} \rightarrow \text{N}_2\text{O}$ in Pseudomonas, and a similar phenomenon in Hamilton Harbour might explain the accumulation of nitrite.

As organic compounds are the energy source for heterotrophic organisms and inorganic compounds such as nitrates serve as electron acceptors, this aspect of the nitrogen cycle interacts to alter the dissolved organic levels in the water. Combined with artificial mixing these processes can improve water colour problems.

C. Turbidity

Hamilton Harbour has moderate levels of turbidity of 1-6 FTU as illustrated in Figure 12. These values are low considering the high vertical attenuation coefficients (\ln units m^{-1}) recorded during 1975 of (0.52-1.58). Although turbidity is to some extent dependent on phytoplankton concentrations, there is a poor relationship between chlorophyll a and turbidity. There is an increase in turbidity during the mixing period, probably as a result of suspended sediment. This observation was confirmed by microscopic analyses which indicated an increased number of empty diatom frustules which had been lifted off the sediment. Despite the increased turbidity, there was actually a decline in the vertical attenuation coefficient suggesting that water color problems were reduced by the mixing processes.

BIOLOGICAL RESPONSES

Unknown environmental synergisms affecting biological production constrain predictions. Predictive models of biological responses have assumed that changes in light or nutrient availability are the dominating factors. In such models, there is no consideration of the stress of a changing environment or adaption of organisms to mixing.

For many species, artificial mixing results in increased habitat volumes for exploitation. Some organisms, however, such as cold water fishes have their habitats destroyed and are selected against by such procedures. In optically deep waters, complete vertical circulation can basically negate phytoplankton production, yet in optically shallow waters circulation enhances phytoplankton production. These are the principal considerations to be resolved when artificial mixing is undertaken.

Perhaps the most important aspect of artificial mixing are the induced changes in the bacterial populations. The composition, distribution and abundance of bacterial populations in Hamilton Harbour have strong effects on the harbour's water quality. Despite this importance, the response of bacteria to artificial mixing has generally been poorly documented. Nutrient cycles, biological oxygen demand and total biological production are dependent on the bacterial content of Hamilton Harbour. Because of this dependency, it is essential to determine what changes in the structure of the bacterial communities result from artificial mixing.

During 1975, total coliform, fecal coliform, fecal streptococci, *Pseudomonas*, heterotrophs, *Nitrosomonas*, sulphate reducers and sulphur oxidizers were determined. Populations were monitored at four stations, samples being collected at the surface and at one meter from the bottom of the water column. As station 258 was located near the diffuser and was representative of the central basin of the harbour, it was selected to be indicative of the effects of artificial mixing.

Figures 13a and 13d illustrate comparative and absolute changes within the communities. It is noted that total and fecal coliform counts are higher for the epilimnetic than the hypolimnetic waters (Figure 13b and d). This is to be expected since the warm sewage effluent will tend to flow over the cooler hypolimnetic waters. As the hypolimnetic waters contain populations which are often within the limits for total body contact recreation one expected result of a good period of artificial mixing would be to "dilute" surface concentrations. On July 31, during the period of most intensive mixing, there was a decrease in surface and

bottom bacteria counts. It is not known if the decrease in concentrations was a direct response to artificial mixing (i.e. dilution) or was an indirect response (initial change in the chemical environment with a secondary response by the bacteria). The latter explanation was accepted as even the hypolimnetic populations decreased, an observation not accounted for by the dilution theory.

There was a decline during the mixing period in the population size of the various monitored taxons excluding the sulphur oxidizers. This response was not confined to station 258, as stations 4 and 252 revealed declining populations at the same time with only sulphur oxidizers being abundant. Station 270 did not indicate a similar trend.

Thiobacillus thioparus (sulphur oxidizer) became less abundant during the onset of destratification and the development of anoxic conditions. During July, at Station 258, there were increases in numbers during the entire period of artificial mixing. It is expected that some aspect of this physical-chemical environment have been modified to increase the growth potentials of T. thioparus. Whether the changes in Eh as outlined in Figure 5 were associated with this modification is not known, but it would appear that minimal mixing can produce desired changes within the bacterial population.

Most studies on eutrophication emphasize the response of phytoplankton to increased nutrient loads. Artificial mixing has been reported to increase phytoplankton standing crop (Hooper et al, 1953; Johnson, 1966; Fast et al, 1972) in some instances, and reduce the size of standing crops in others (Lackey, 1971; Ridley, 1972). These apparently conflicting findings ensue from the variety of applications of mixing.

Algal productivity during mixing has been studied by Fast (1971) and Haynes (1975). Although it has been generally agreed that primary productivity increases during mixing periods because of improved nutrient availability and light penetration, there are times where decreased productivity occurs especially when associated with deep vertically circulated water columns. Mixing depth is a critical factor when managing algal production. Talling (1971) and Murphy (1962) noted reductions in standing crop occur when the mixing depth is greater than the compensation depth at which the rate of photosynthesis equals the rate of respiration. Toetz (1972) speculates that artificial mixing accelerates both the rate of energy flow and nutrient cycling.

Productivity measurements in Hamilton Harbour were performed by Dr. G. Harris of McMaster University. Table 1 presents strong evidence to suggest that high phytoplankton productivity was associated with the onset and end of the mixing period.

Table 1: Calculated Assimilation Numbers Determined in Hamilton Harbour, Station 270, 1975 (mg. CO₂ mg Chlor. a⁻¹, hr⁻¹).

<u>Date</u>	<u>Assimilation Number</u>
July 7, 1975	5.5
July 14	30.6
July 21	26.7
July 28	15.9
Aug 11	9.1
Aug 18	30.5
Aug 25	8.3

Productivity at Station 270 was initially very high on July 14 with only one diffuser line operating. During July, there was a decline in the assimilation numbers perhaps reflecting nutrient utilization (nitrate depletion was observed on one occasion during July), or increased depth of vertical mixing as there was a definite tendency for Station 270 to tend toward the continuous temperature gradient during this period of mixing.

Phytoplankton standing crop was determined by staff of Water Modelling Group by direct microscopic counts using the Utermohl technique with split sedimentation chambers. Chlorophyll a measurements were made to support the microscope data as chlorophyll a was not in itself a reliable measure of standing crop.

During the last week of July with all the diffusers operating there was a distant change in the phytoplankton composition and abundance. In late June to early July Lagerheimia longiseta (lenn.) Printz. was replaced by Oocystis borgei Snow. and Rhodomonas minuta var. nannoplanctica Skuja. These species dominated the phytoplankton until late July when a large, relatively isolated growth of Ankistrodesmus falcatus (Corda) Ralfs. and possibly Ankistrodesmus braunii (Naeg.) Brunn. occurred. A third species became common during this period and was tentatively identified as Kirchneriella spp. (see Figure 14).

Calculated algal volumes on July 28 were $8.0 \times 10^7 \text{ cm}^3 \text{ ml}^{-1}$, a peak for the entire survey. It should be noted, however, that the chlorophyll a data do not illustrate this (see Figure 15a). This indicates that chlorophyll is not a consistent estimate of standing crop unless supported by other techniques.

Artificial mixing altered the periodicity, abundance and composition of phytoplankton standing crops. Although it is unlikely that phytoplankton were responding to changes in the mixing regime, they might well have been responding to secondary effects such as nutrient availability. The pulse of Ankistrodesmus was of short duration and erratic distribution as it was not abundant at Station 252 or 270. This type of response suggests that the effects of artificial mixing were more noticeable in the deep water stations, and might have had little effect in the shallow stations which can be destratified at any time during the summer should wind mixing be sufficient.

Determining the effects of artificial mixing on zooplankton populations would involve determining the modifications resulting from changes in temperature, dissolved gases, light, predation and competition. Fast (1971) concluded that destratification extended the vertical distribution of zooplankton. This is similar to the situation in Hamilton Harbour, as a peak zooplankton biomass (0.0389 m^{-1}) occurred during July 21-July 28. It would be dangerous to attach too much significance to this peak, as the temporal and spatial distribution of zooplankton exhibited marked fluctuations (Fig. 16). Volume samples collected by McMaster University indicated that zooplankton populations were vertically extended.

In some circumstances, aeration has resulted in species indicative of more oligotrophic conditions becoming common (Linder and Mercier, 1954), but this did not occur in the harbour. There can be little doubt that the mixing project did, in fact, increase the habitat boundaries of the zooplankton. The composition of the populations is basically dominated by rotifers, with cladocerans and copepods being relatively scarce. McNaught et al (1975) has observed that many cladocerans such as Daphnia and Bosmina tend to be rare in urban and industrial areas.

Zooplankton and fish populations are expected to have a slow response to artificial mixing. Artificial mixing is becoming very common in the fisheries aspect of lake management (Hooper et al, 1953; Grim, 1952; Fast, 1966, 1971; Irwin et al, 1967; and Lackey, 1971). The habitat of fish is basically determined by food availability, but as stratification occurs, the lake strata of desirable temperature and dissolved oxygen content are decreased and this contracts the viable habitat volume. Summer die-off is related to anoxia, limited algal production, algal toxins, and fungal diseases; situations which are altered by artificial mixing. As noted in the section on temperature and dissolved oxygen, there was not sufficient change in these parameters to result in increased fish habitat.

With regard to Hamilton Harbour, a fish netting by the Ministry of Natural Resources found a relatively low abundance of fish. Nettings in July were completely unsuccessful indicating that the vertical habitat of fish was not extended. Until dissolved oxygen content increases to 3-5 mg/l for a long period of time, and toxic dissolved gases such as ammonia and hydrogen sulphide become less abundant, there can be little or no change in the fish population. It is of value to note that in a body of water as anoxic as Hamilton Harbour, destratification would probably deplete the fish population. A rapid intrusion of anoxic hypolimnetic water would result in the suffocation of the resident fish population. It is because of this, artificial mixing must be on a slow basis and destratification not be a desired situation. By preventing stratification or by lowering the rate at which column stabilization is increasing, artificial mixing can prevent such stress situations.

SUMMARY AND FUTURE CONSIDERATIONS

The period of artificial mixing of Hamilton Harbour was too short to have ameliorated any water quality problems for any appreciable length of time. The 1975 mixing experiment was not seeking destratification as an end goal, but rather to relieve the condition and symptoms of hypolimnetic anoxia. Secondary effects of this aeration aspect would indicate that the aeration can actually increase the assimilation potential of the harbour. This study confirms Toetz's (1972) hypothesis that mixing enhances energy flows within the system, and if the data to date concerning the relation of artificial mixing to improved water quality are an accurate guide, mixing will be beneficial for immediate problems and perhaps corrective in the long term.

Artificial mixing will be continued in Hamilton Harbour in 1976. Repositioning of the aerator lines to extend from the north wall of Stelco will minimize damage from ships. The actual diffuser sections would be in the same deep basin, and the lines would cross the shipping lanes in deep water.

The responses of Hamilton Harbour to artificial mixing were:

1. Mixing of hypolimnetic and epilimnetic waters without destratification.
2. Increased dissolved oxygen concentrations, but as a result of the short period of mixing there was little change in the dissolved oxygen budget.
3. Although no direct changes were determined with heavy metals, this can be considered as a positive response, as one of the problems of artificial mixing is a resuspension of heavy metals adhered to fine particles. There appears to be some increase in turbidity but this

is quite likely related to algal biomass and small amounts of resuspended sediments. There were no indications of precipitation of oxides of the heavy metals monitored.

4. There was little change in alkalinity, pH or conductivity. The only component of conductivity which is theoretically expected to change is calcium, but this was not observed in practice.
5. Changes in nutrient concentrations and distributions were suspected because of changes in algal productivity. Vertical distributions of total phosphorus were altered. Hypolimnetic filtered reactive phosphorus increased suggesting that sediment release was possibly occurring during the mixing period.
6. Bacterial populations generally declined during the period of intensive mixing, but showed no response when only two diffusers were operating. Sulphur oxidizers responded in a manner indicating that mixing favors their production.
7. Zooplankton extended their vertical habitat but had little change in composition. There was no measured response by the fish population to the brief period of mixing.
8. Increased phytoplankton production and standing crop.
9. Sediment oxygen demands remained sufficiently high to maintain an oxygen stress situation throughout the harbour. Selective sediment removal is suspected to cause temporal stress situations by increasing the dissolved oxygen demand and turbidity.

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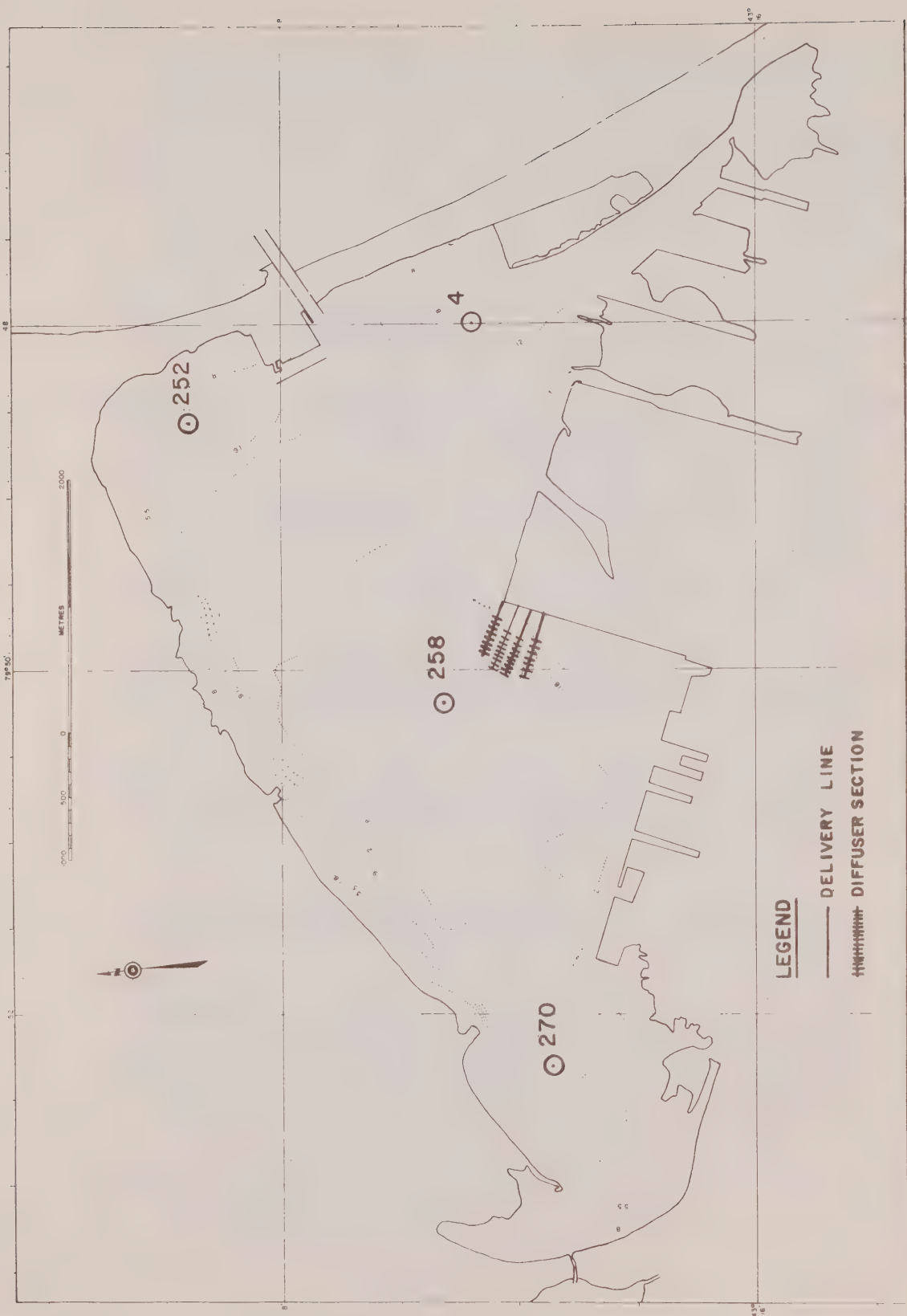


FIGURE 1: HAMILTON HARBOUR ARTIFICIAL MIXING SYSTEM & SAMPLING STATIONS

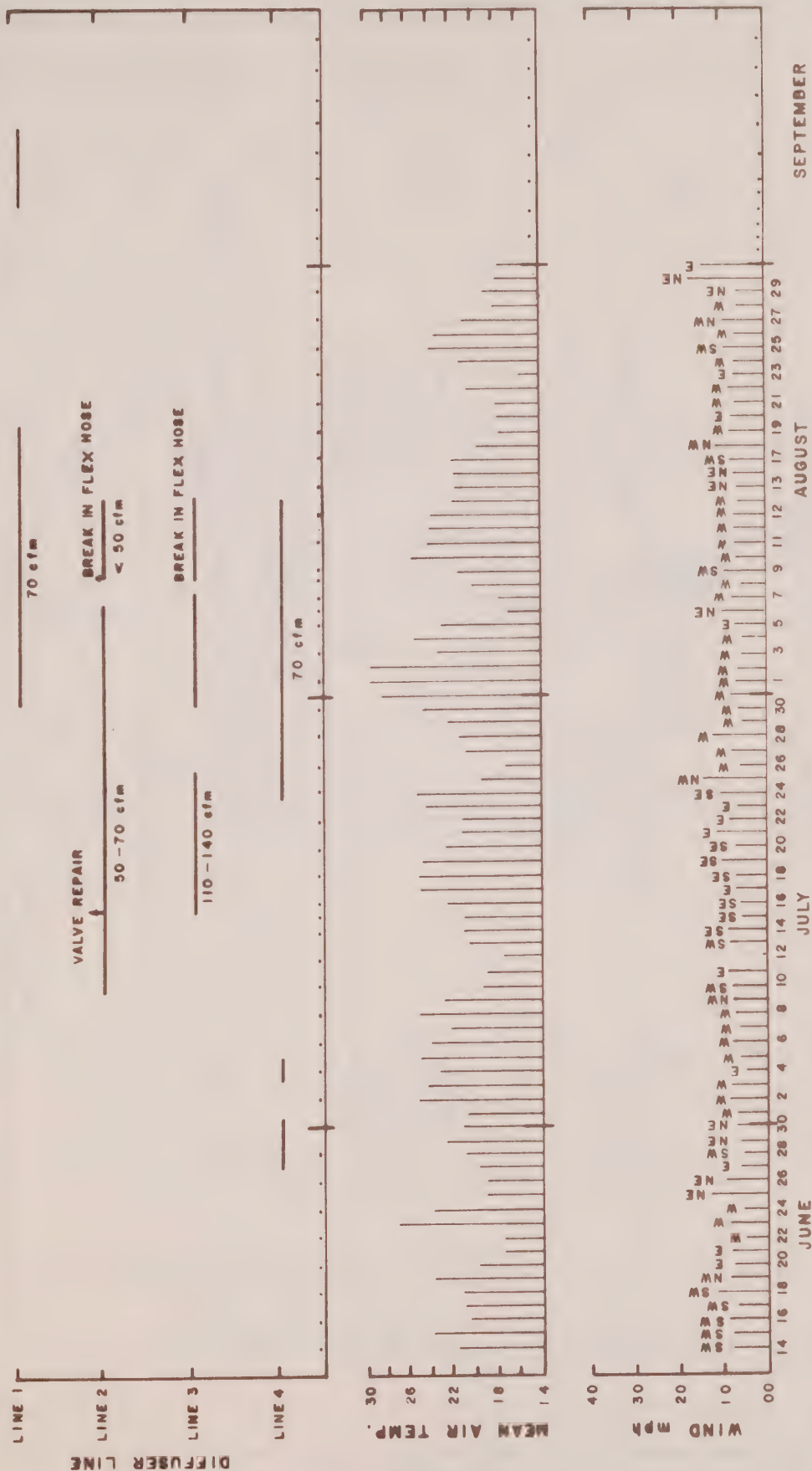


FIG. 2 OPERATION OF DIFFUSER LINES WITH AMBIENT WIND AND MEAN TEMPERATURE DATA.

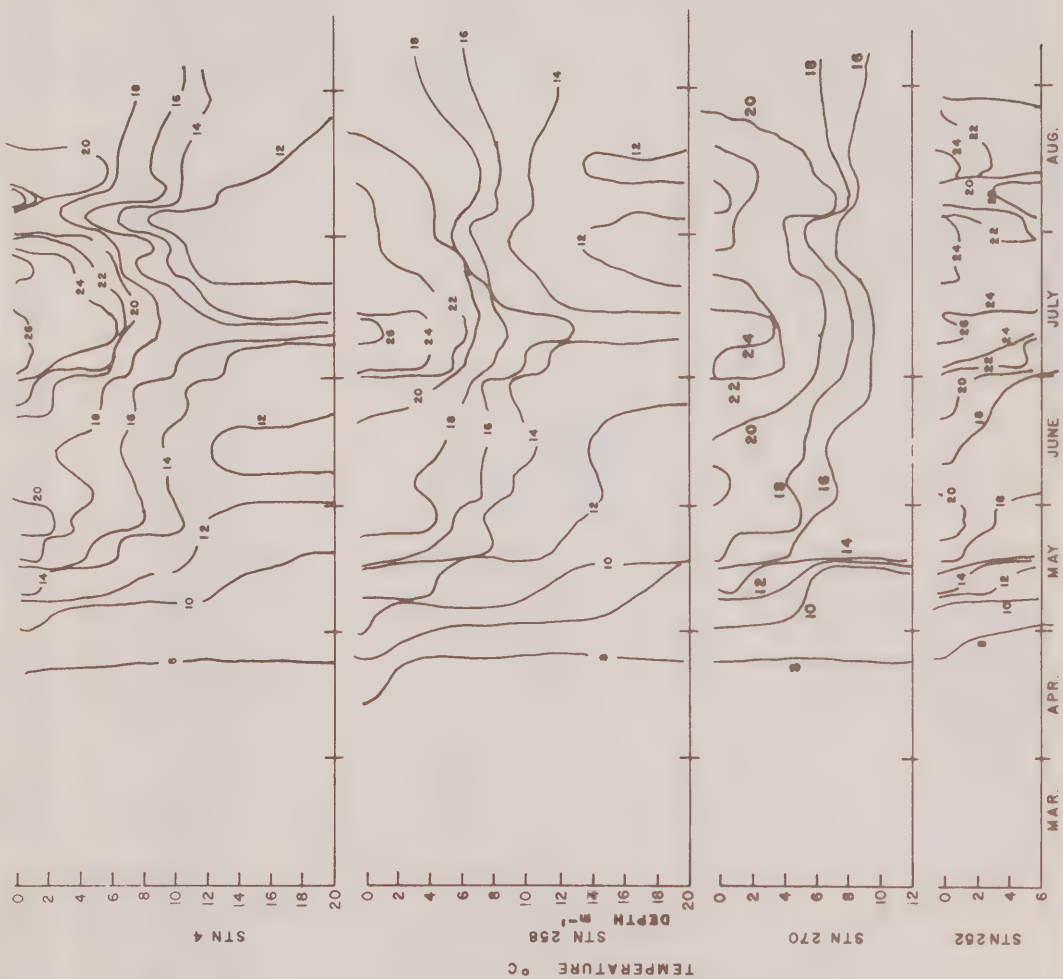


FIG. 3 THERMAL ISOPLETHS °C AT STATIONS 4, 258, 270, AND 252.



FIG. 4 DISSOLVED OXYGEN - DEPTH PROFILES DURING THE MIXING PERIOD. (mg/l).

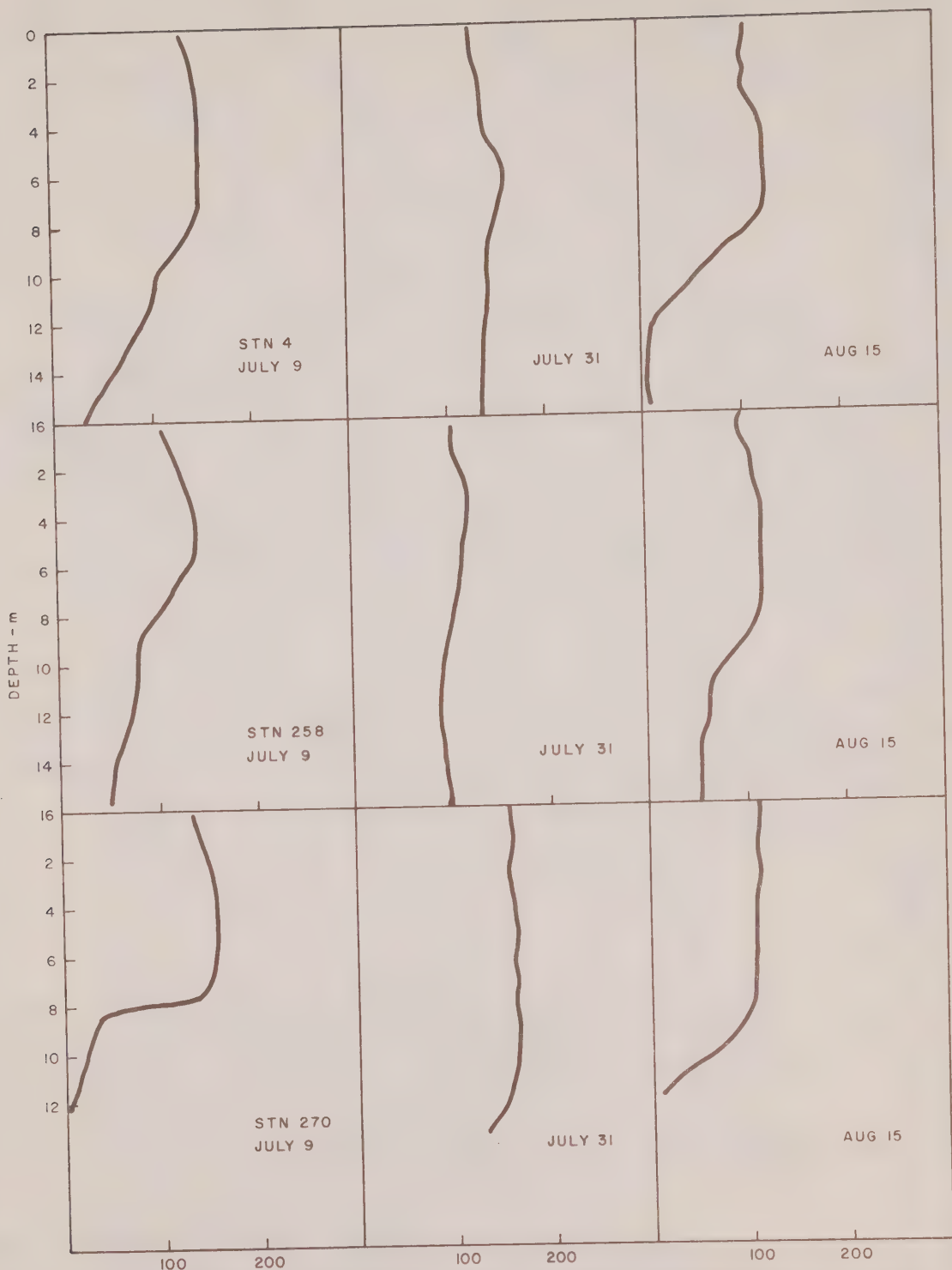


FIG. 5 REDOX POTENTIAL (mv) - DEPTH PROFILES DURING MIXING PERIOD.

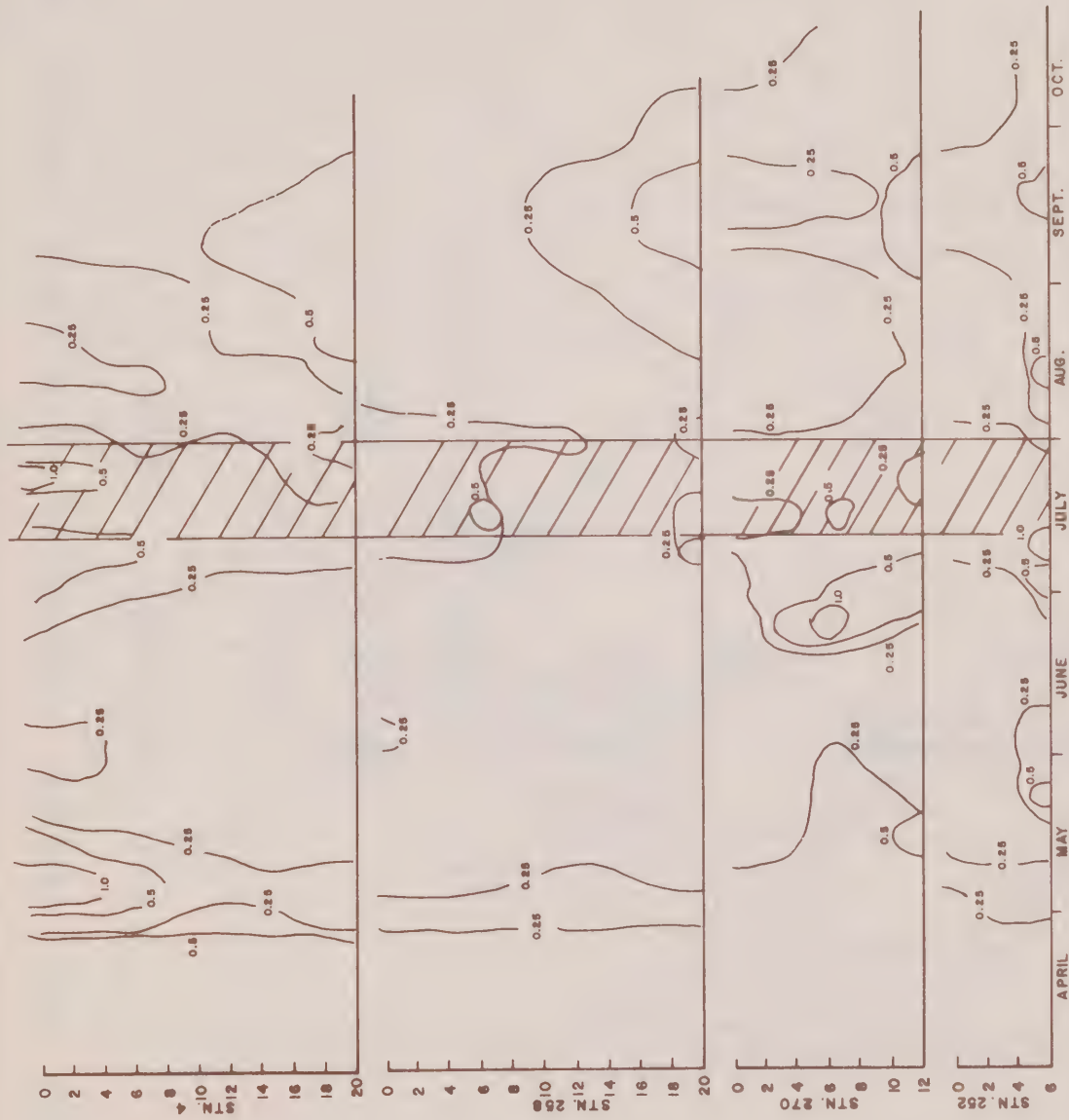


FIG. 6 VERTICAL AND TEMPORAL DISTRIBUTION OF IRON (mg/l) AT STATION 4, 258, 270, AND 252.

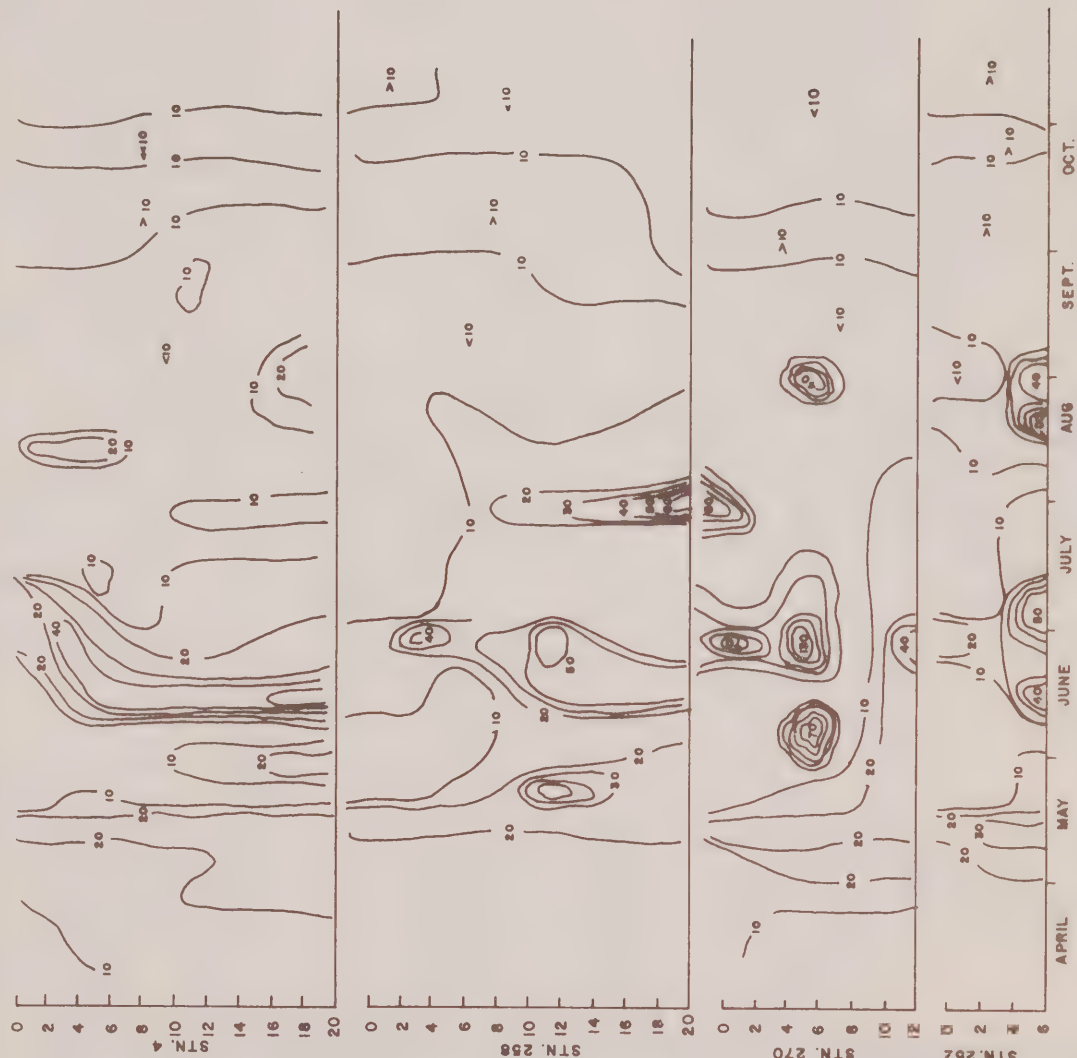


FIG. 7a VERTICAL AND TEMPORAL DISTRIBUTION OF SOLUBLE REACTIVE PHOSPHORUS ($\mu\text{g/l}$)

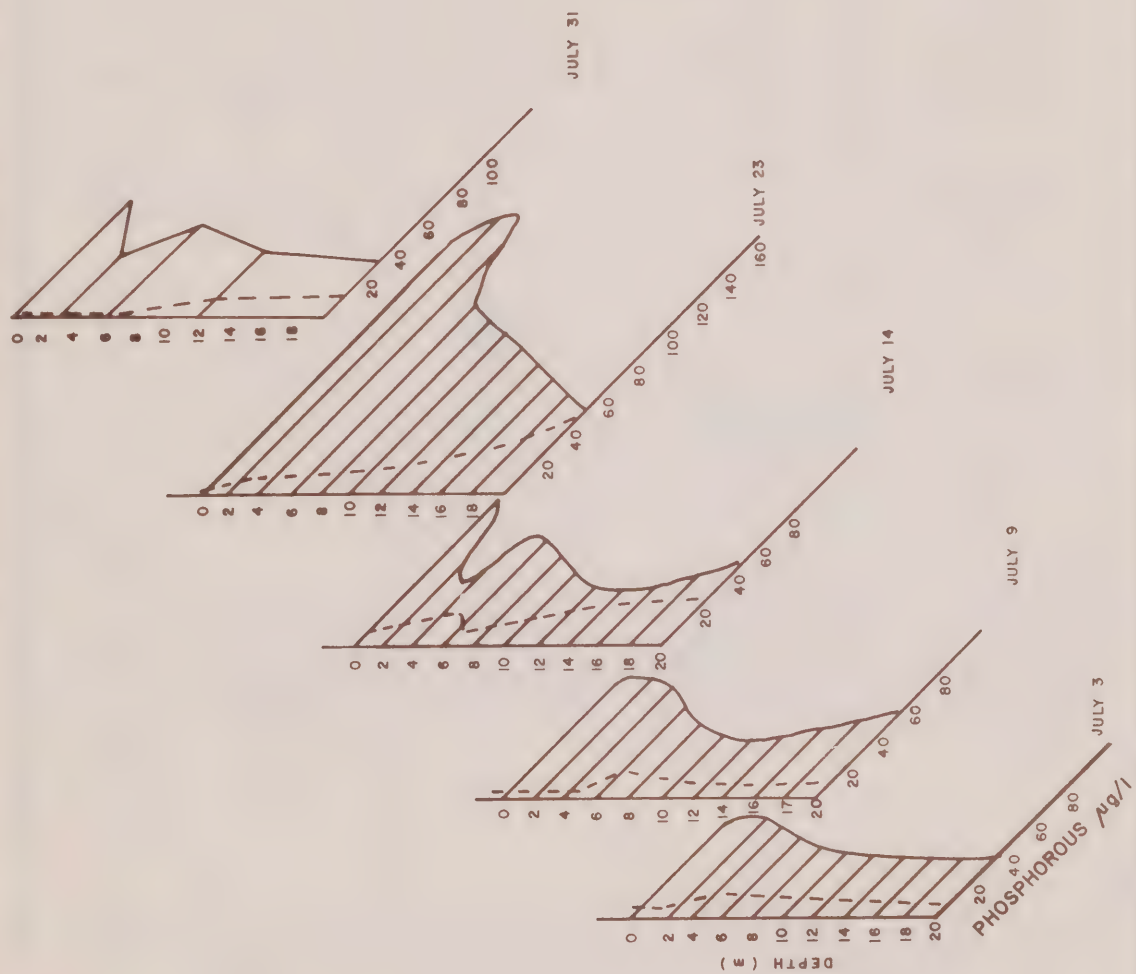


FIG. 7b VERTICAL DISTRIBUTION OF TOTAL (—) AND FILTERED REACTIVE PHOSPHORUS (---) AT STATION 258.

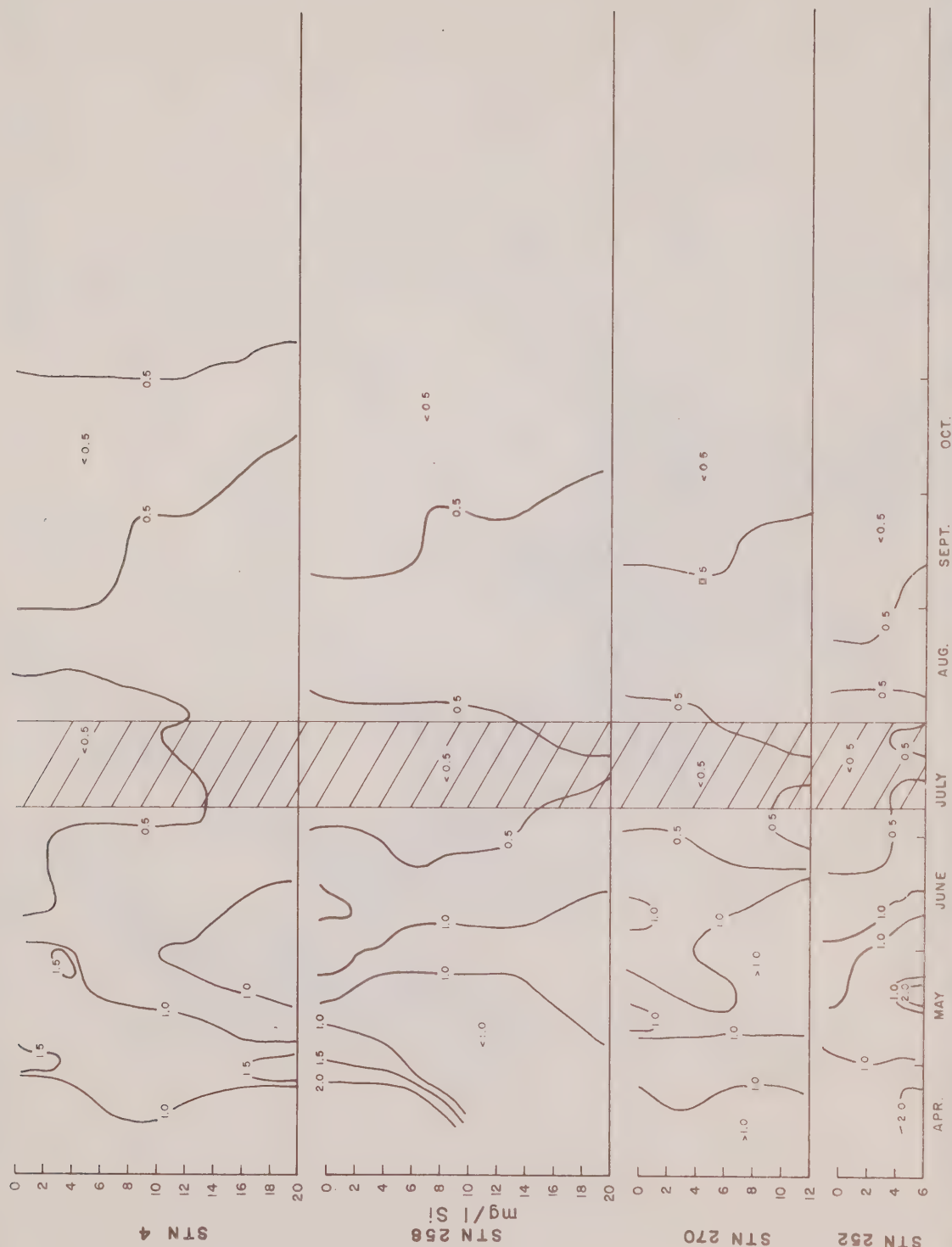


FIG. 8 VERTICAL AND TEMPORAL DISTRIBUTION OF DISSOLVED REACTIVE SILICATES (mg/l) AT STATIONS 4, 270, 258, 252, 1975.

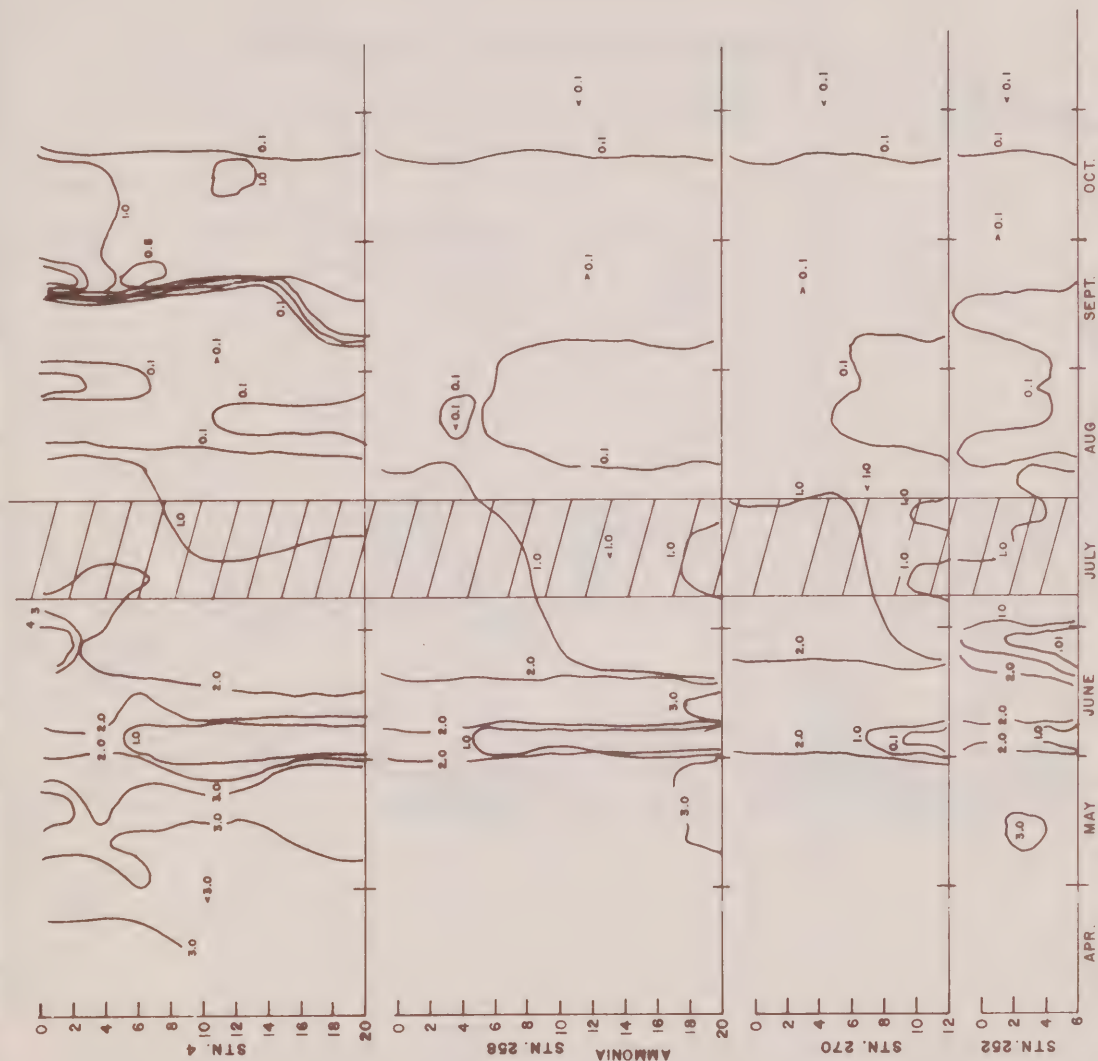


FIG. 9 TEMPORAL AND VERTICAL DISTRIBUTION OF NH_4 (mg/l).

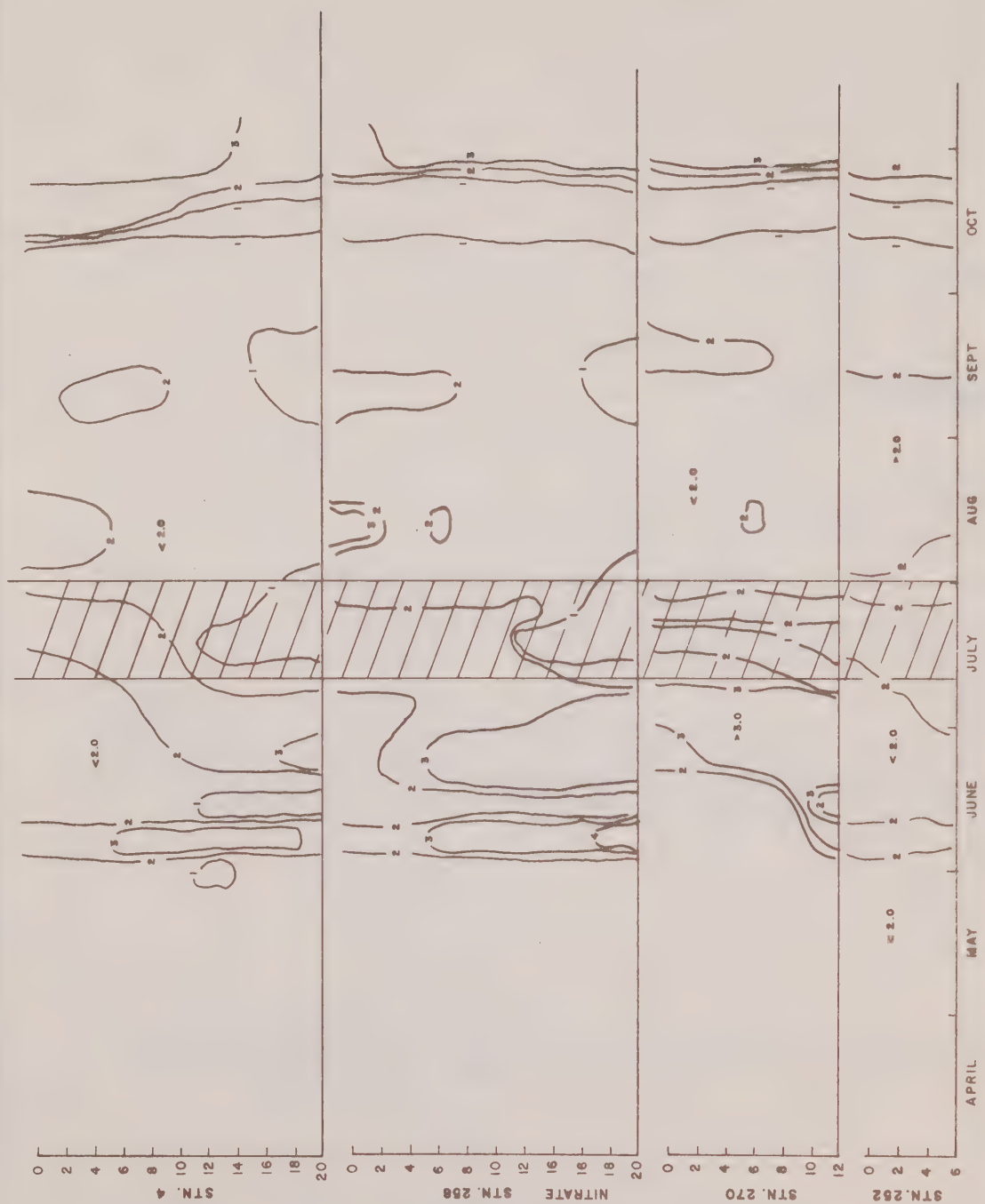


FIG. 10 VERTICAL AND TEMPORAL DISTRIBUTION OF NO_3 (mg/l) AT STATIONS 4, 258, 270, AND 252.

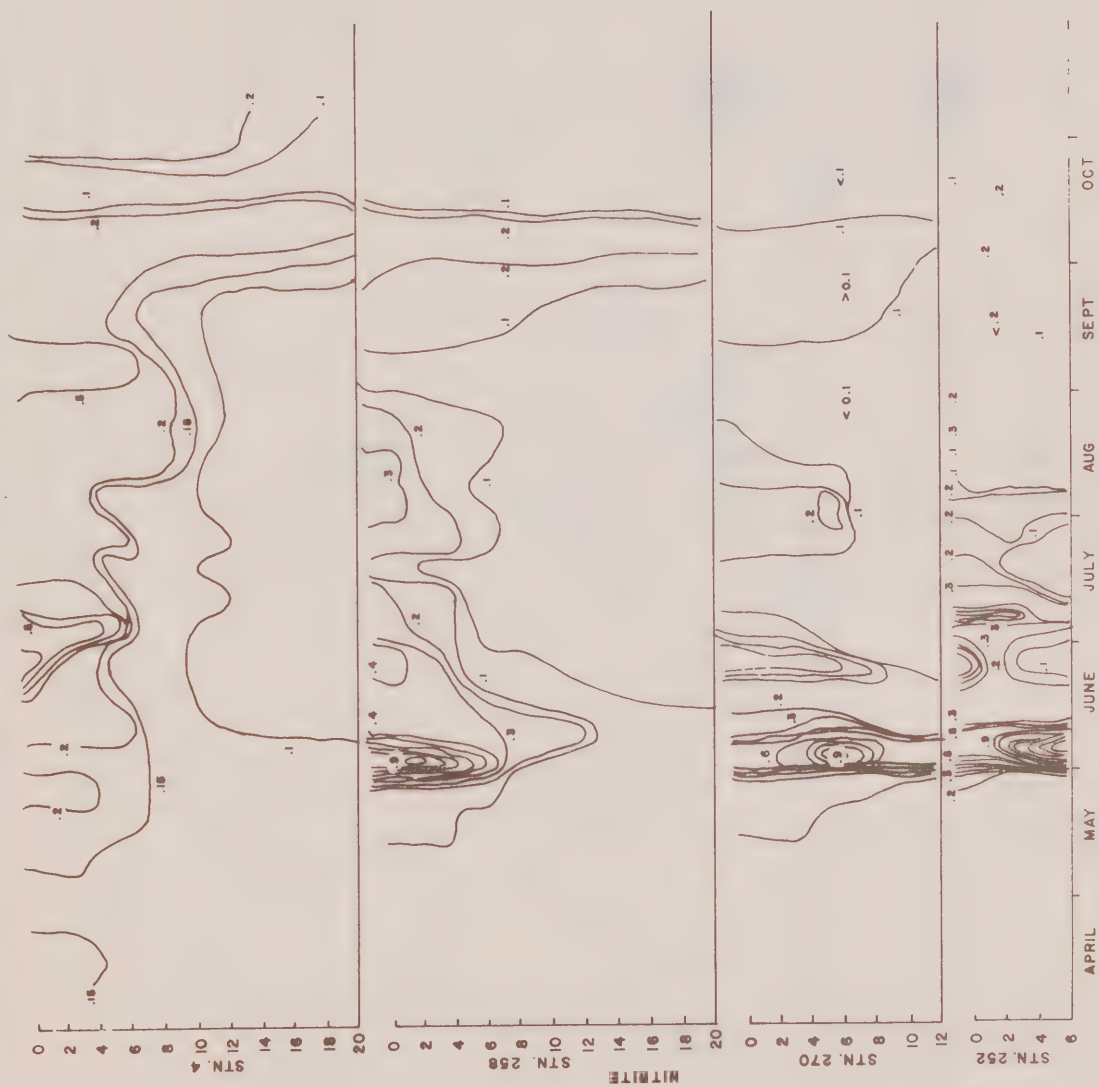


FIG.11 VERTICAL AND TEMPORAL DISTRIBUTION OF NITRITES (mg/l).

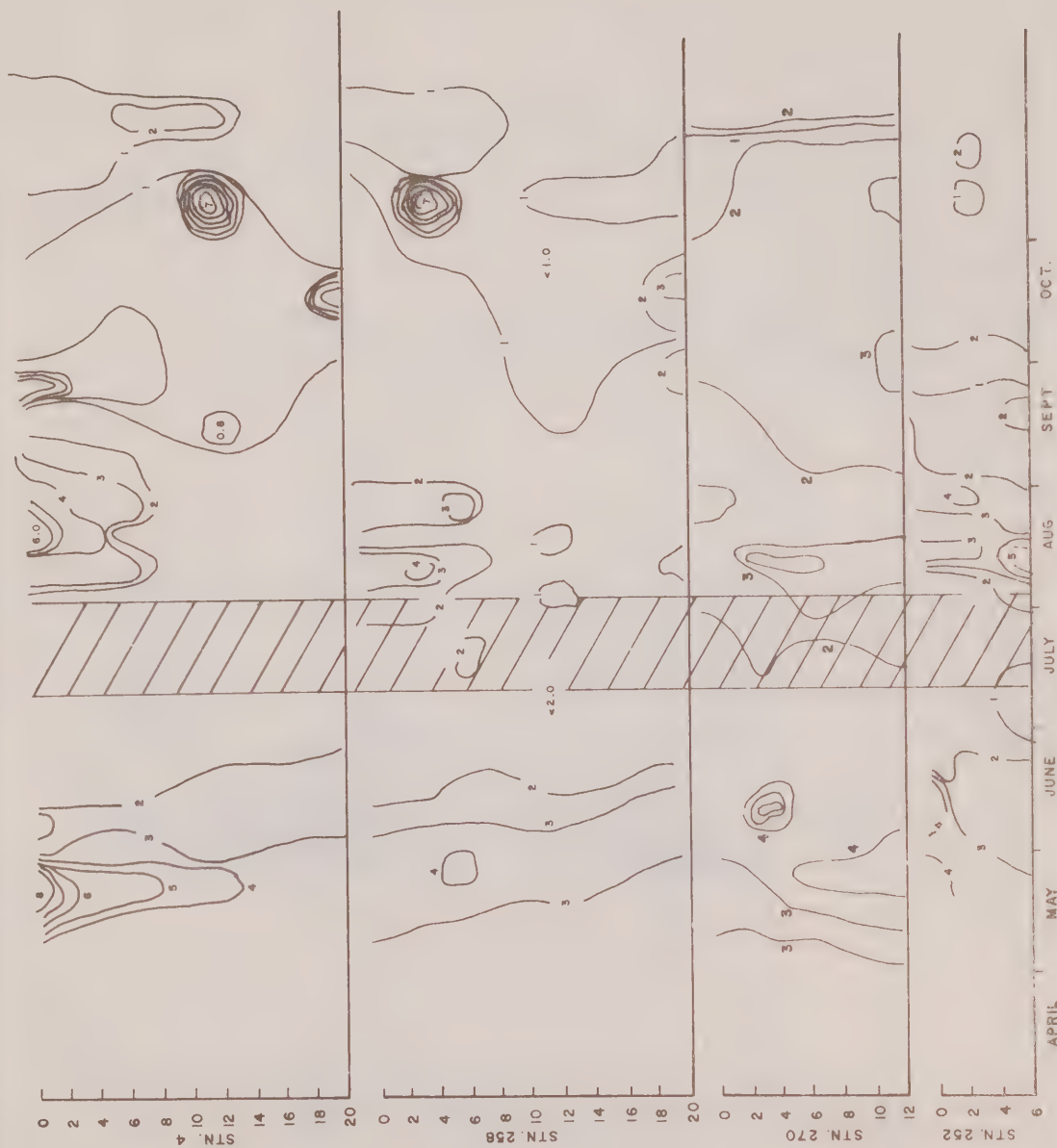


FIG.12 VERTICAL AND TEMPORAL DISTRIBUTION OF TURBIDITY (FTU).

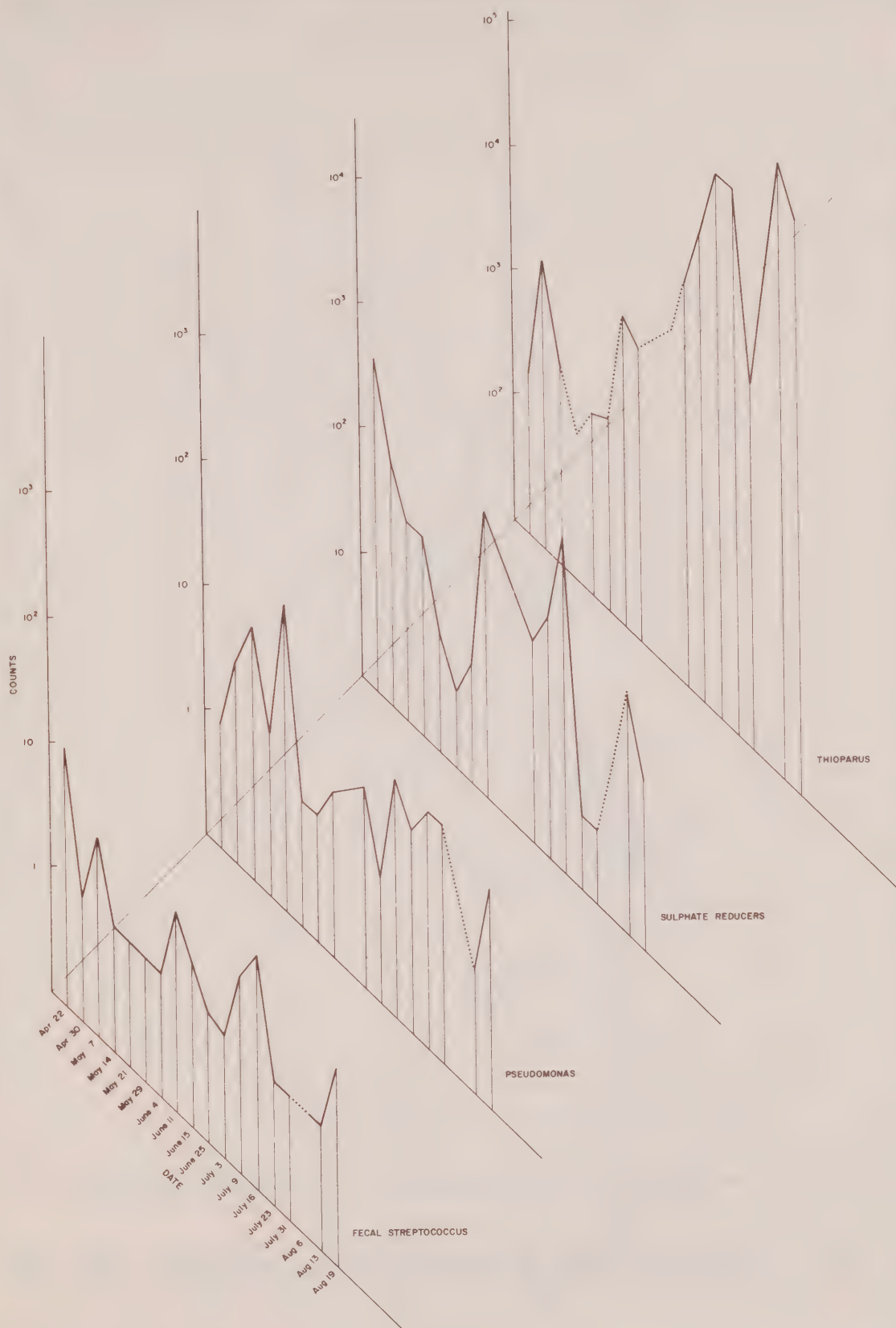


Figure 13a. Bacterial Populations at Station 258, 1975 (surface).

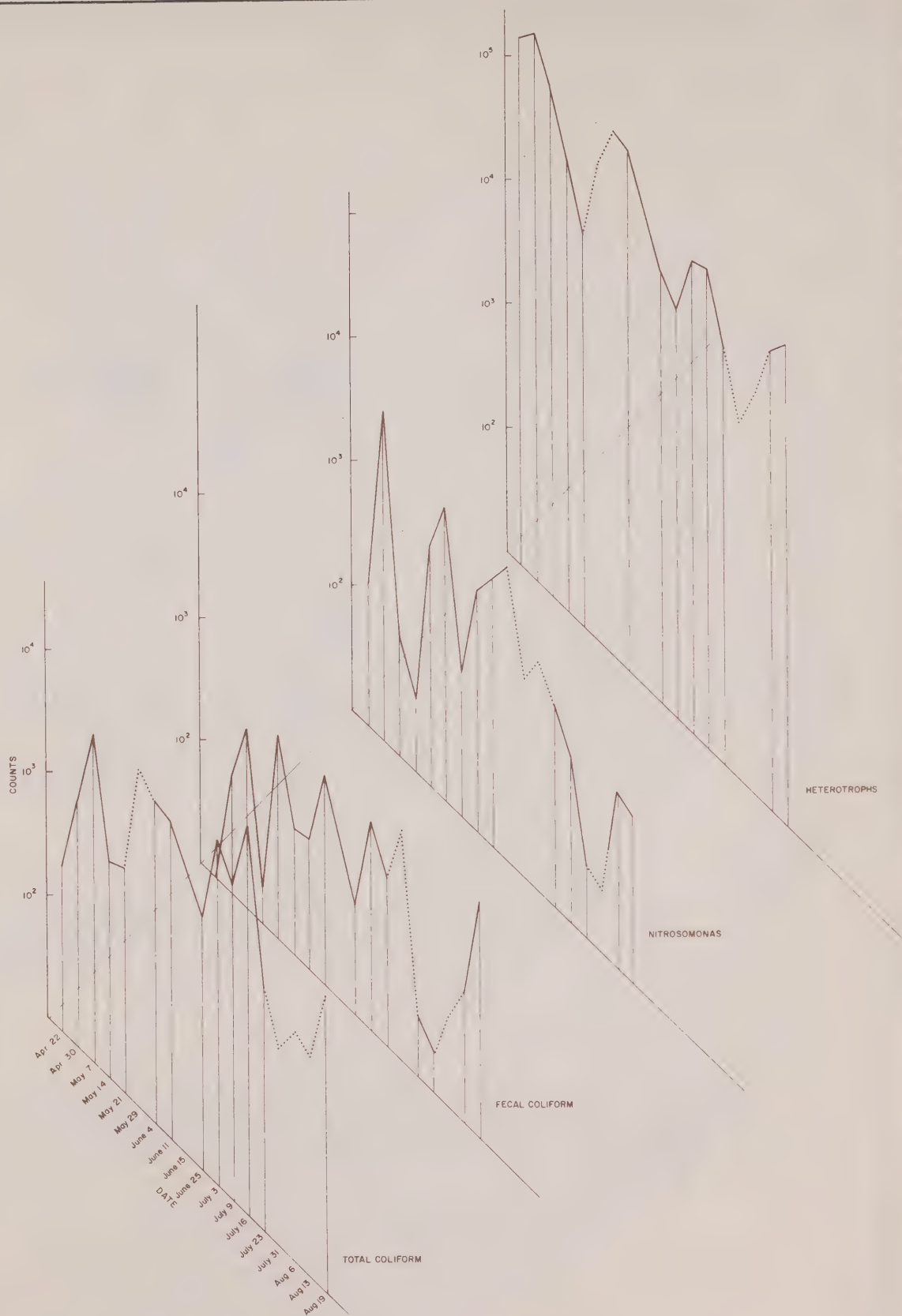


Figure 13 b. Bacterial Populations at Station 258, 1975 (surface).

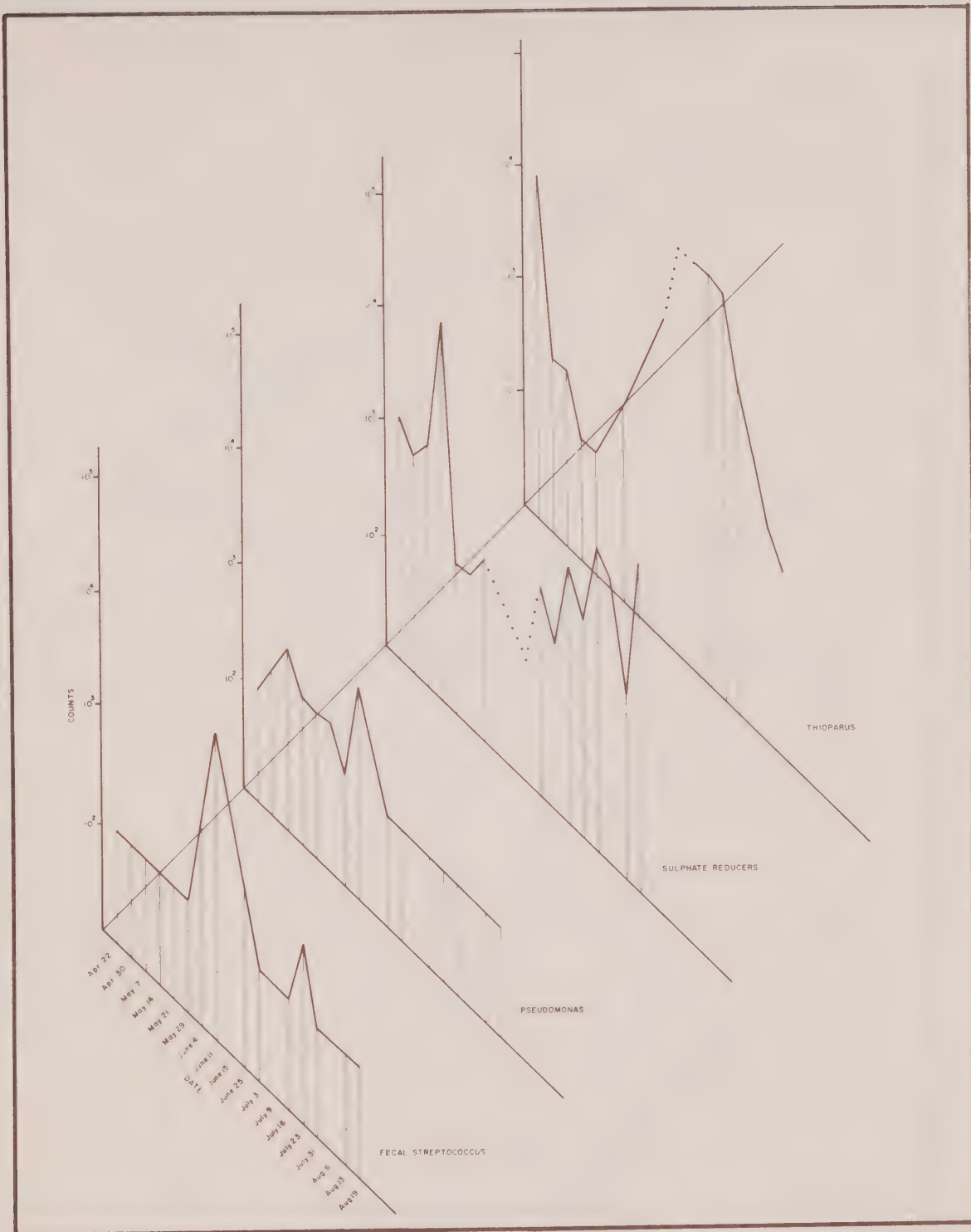


FIG. 13c BACTERIAL POPULATION AT STN. 258, 1975 (BOTTOM).

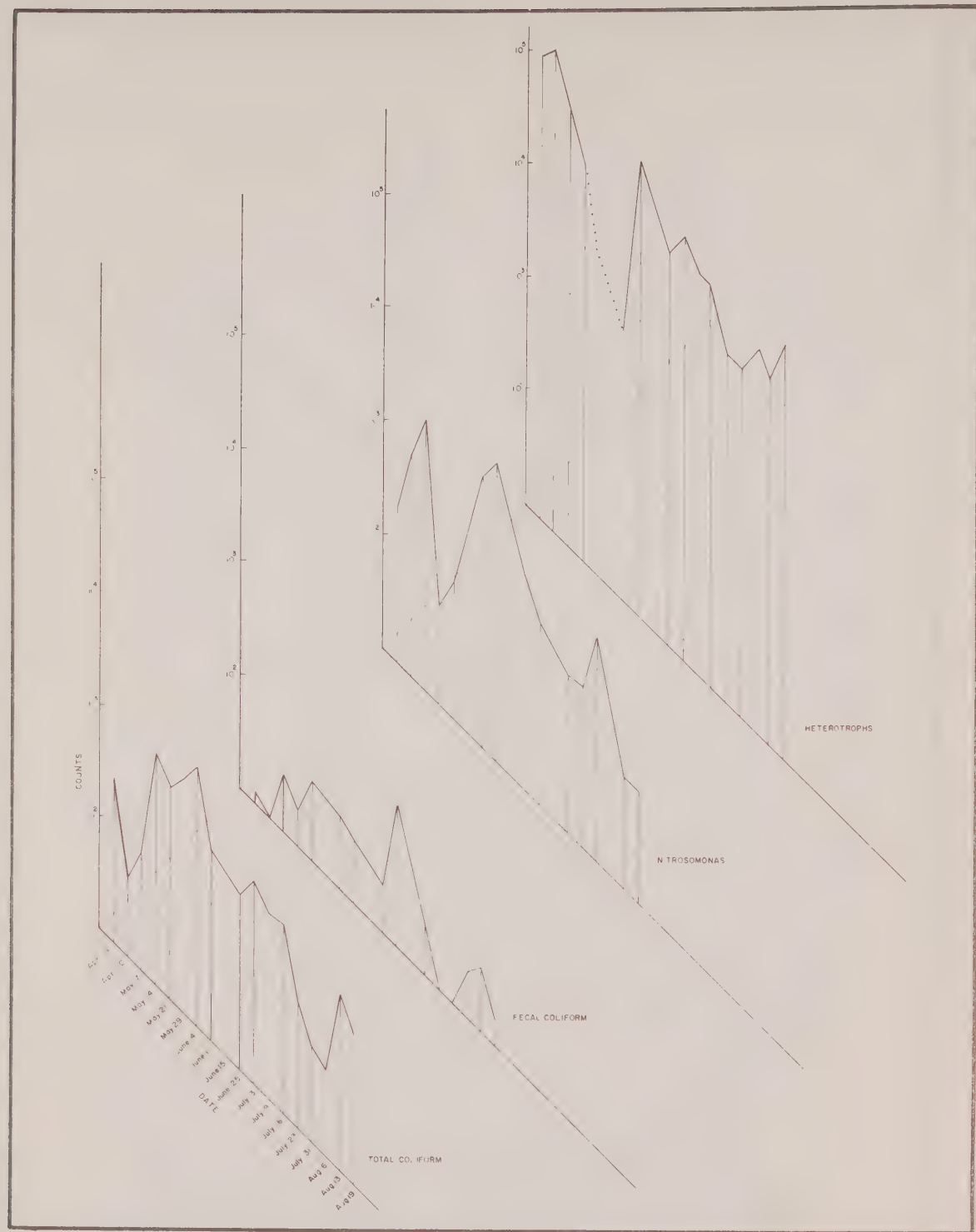


FIG. 13d BACTERIAL POPULATION AT STN, 258, 1975 (BOTTOM).

PHYTOPLANKTON RESPONSE TO ARTIFICIAL MIXING

- A — A *ANKISTRODESMUS FALCATUM*
- F — F *FRAGILARIA CROTONENSIS* & *F. CONSTRUENS*
- K — K *KIRCHNERIELLA*
- O — O *OOCYSTIS BORGEI*
- P — P *PANDORINA MORUM*
- R — R *RHODOMONAS MINUTA*

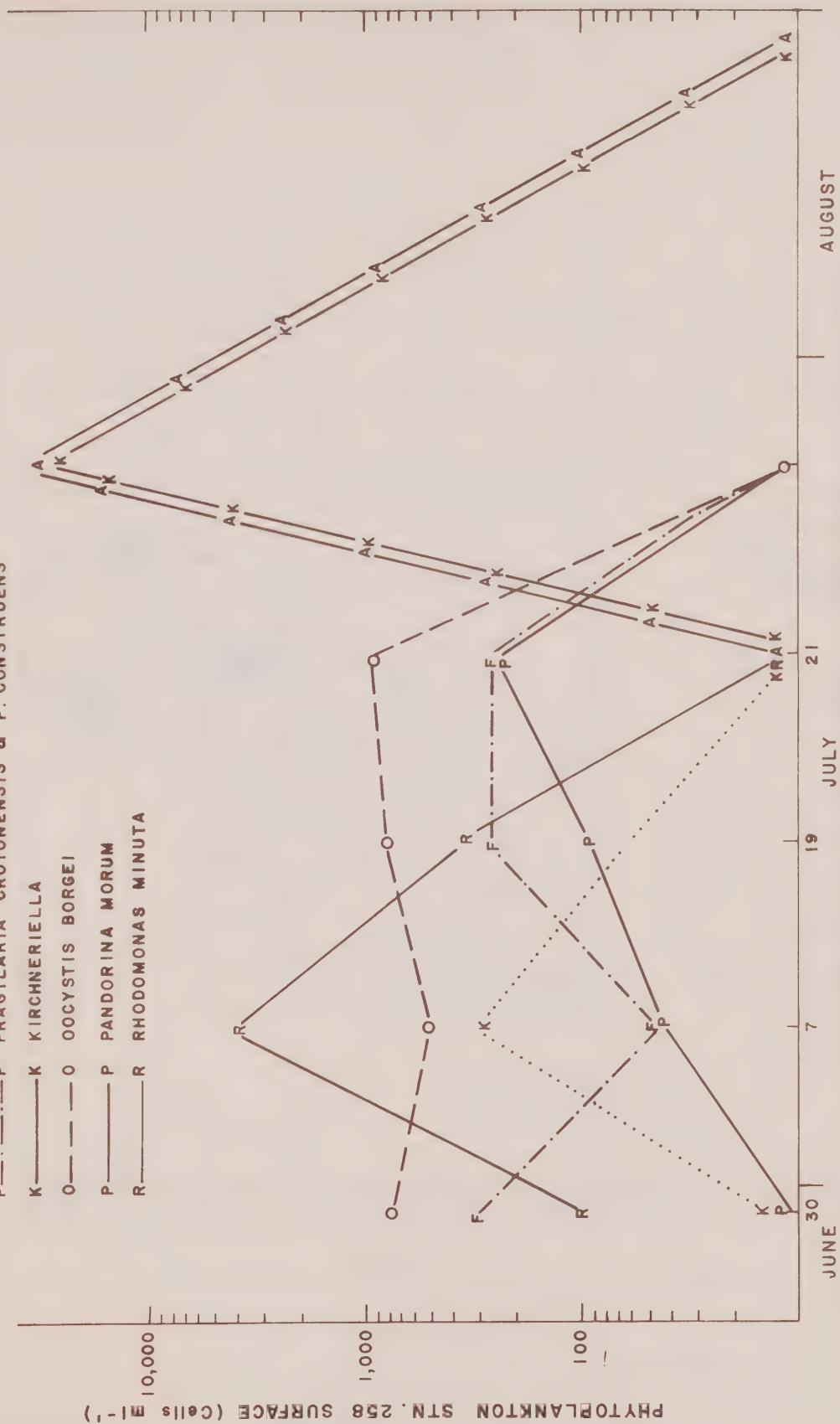


FIG. 14 PHYTOPLANKTON DISTRIBUTION (SURFACE) AT STATION 258, 1975 (CELLS/ml).

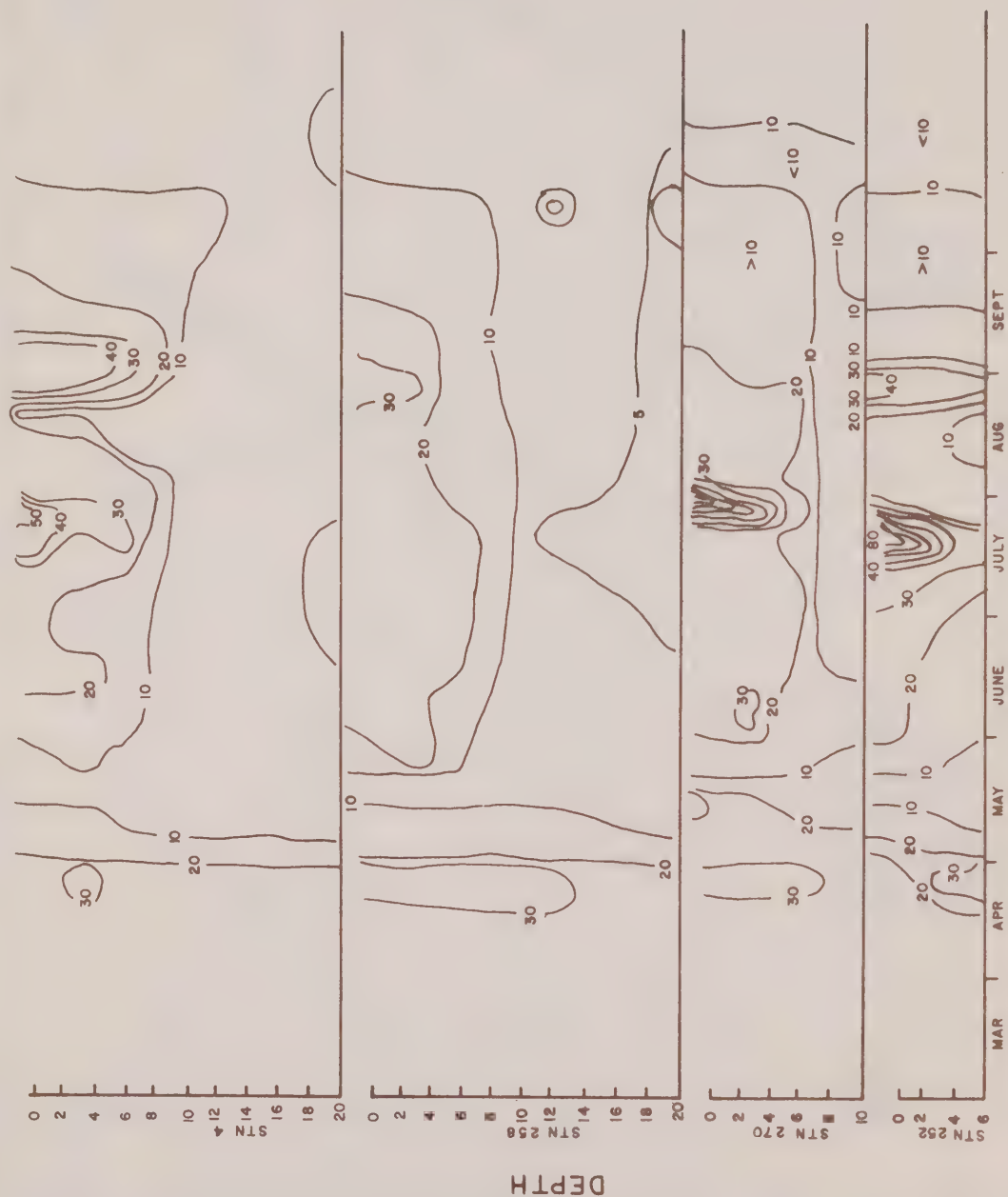


FIG. 15(a) VERTICAL AND TEMPORAL DISTRIBUTION OF CHLOROPHYL "A" ($\mu\text{g/l}$) AT STATIONS 4, 258, 270, AND 252.

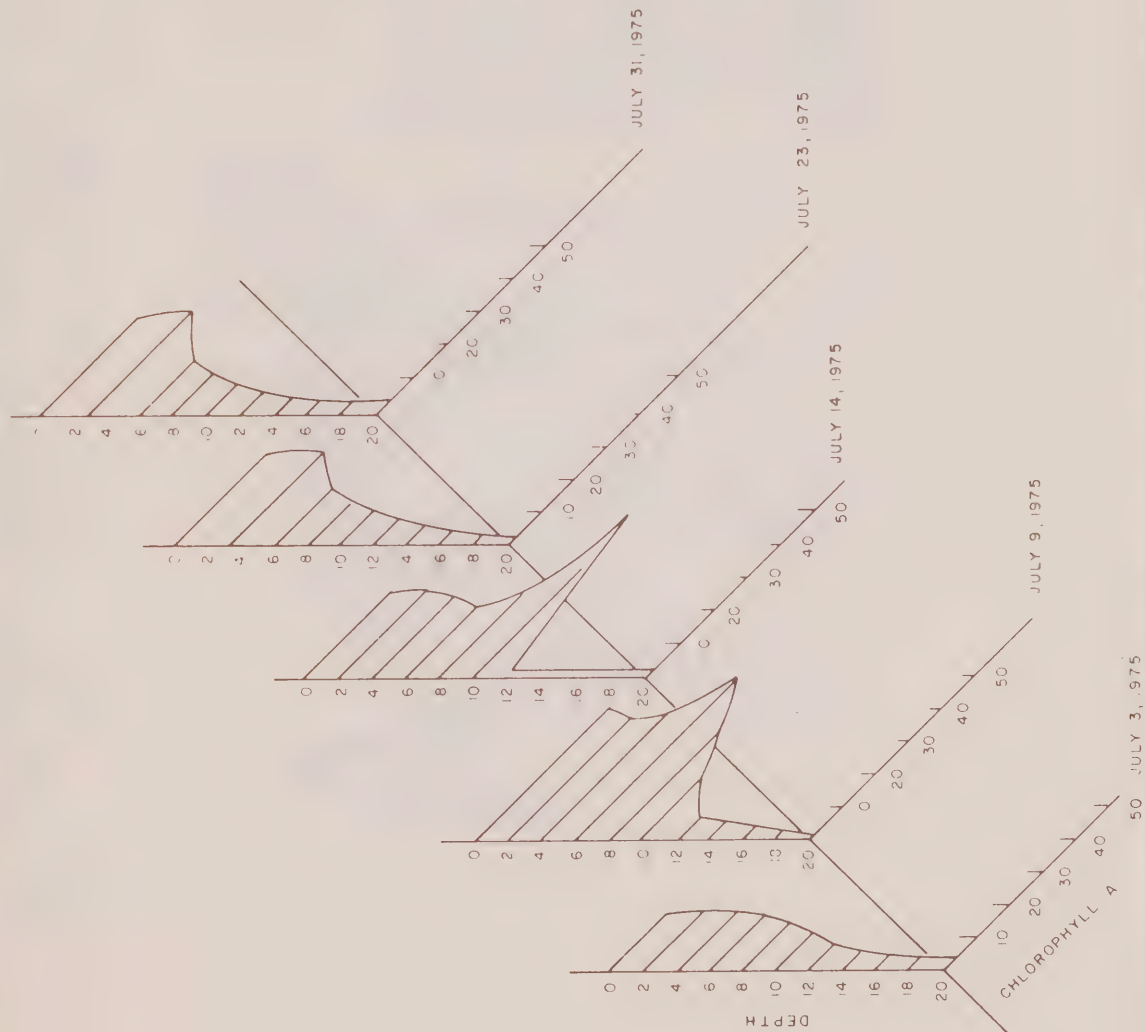


FIG. 15b CHLOROPHYLL DISTRIBUTION DURING THE MIXING PERIOD AT STATION 258, 1975.

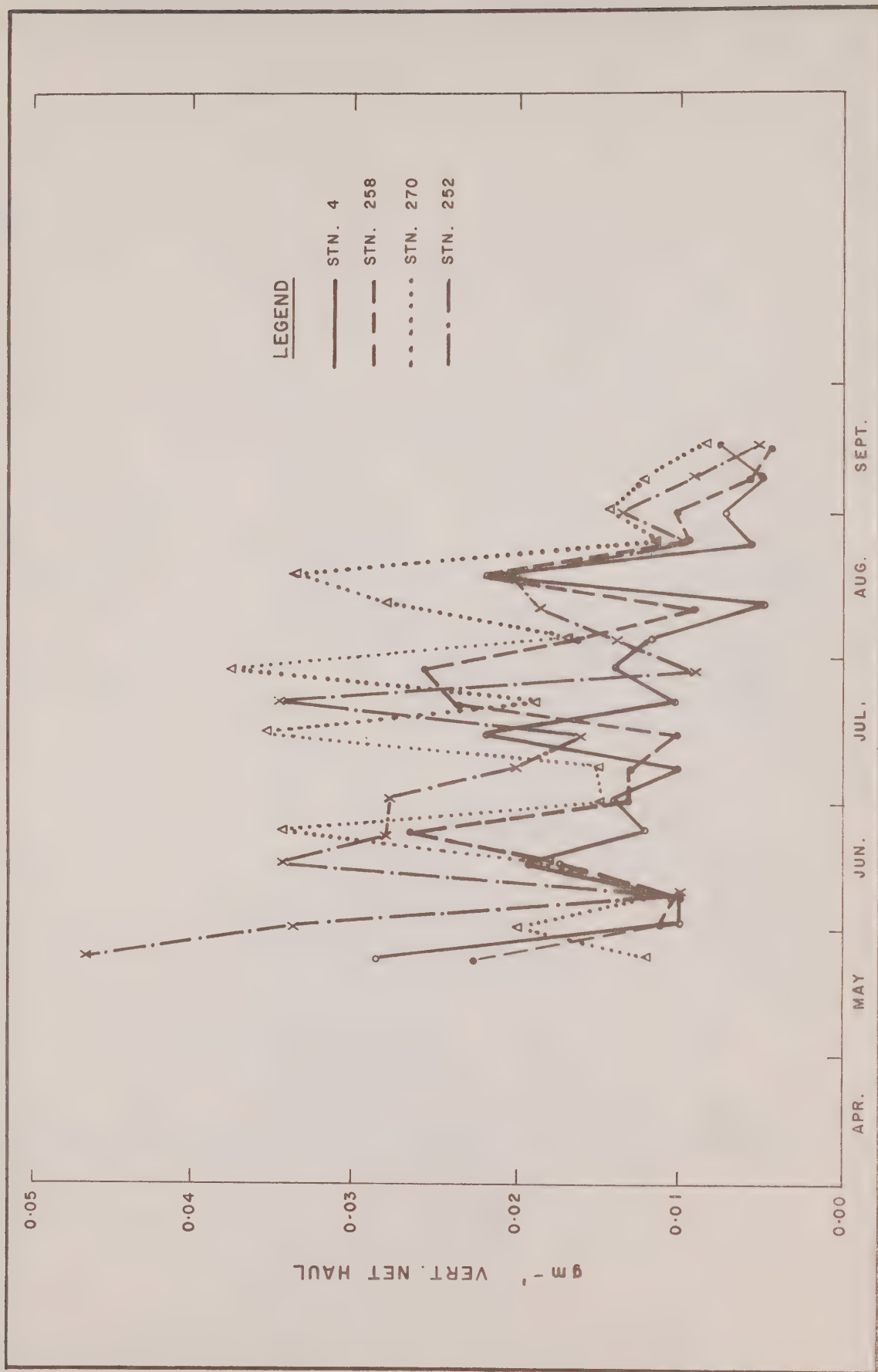


FIGURE 16: RELATIVE ZOOPLANKTON ABUNDANCE (gm.-1 VERTICAL NET HAUL AT STATIONS 4, 258, 270 & 252 - 1975

HAMILTON HARBOUR STUDY '75

section C
Sediments

SUMMARY

SEDIMENT CHEMISTRY

HAMILTON HARBOUR SEDIMENTS CONSIST OF GRAY TO BLACK ORGANIC MUDS IN MOST PARTS OF THE HARBOUR. SANDY OR SILTY SEDIMENTS WERE FOUND ALONG THE NORTH SHORE NEAR THE BURLINGTON SHIP CANAL AND AT THE ENTRANCE TO COOTE'S PARADISE.

THE HIGHEST CONCENTRATIONS OF NUTRIENTS AND HEAVY METALS ARE FOUND IN THE DEEP CENTRAL PART OF THE HARBOUR AND ADJACENT TO THE OUTFALLS. ZINC, CHROMIUM, LEAD AND IRON EXHIBIT LEVELS INDICATIVE OF HEAVY POLLUTION; MODERATE POLLUTION IS OBSERVED ALSO FOR COPPER, NICKEL, MANGANESE, CADMIUM AND MERCURY. THESE METALS EXHIBIT SURFACE TO BOTTOM PORTION ENRICHMENT FACTORS OF 2-6 IN CORE SAMPLES.

THE SEDIMENT DATA WERE ALSO ANALYZED BY THE RATIO MATCHING METHOD USED IN 1974. FACTOR ANALYSIS WAS APPLIED TO THE SIMILARITY COEFFICIENTS TO IMPROVE THE SENSITIVITY TO INDICATE SPATIAL CORRELATIONS. THE RESULTS SHOWED THAT SEDIMENT SAMPLES FROM THE ENTIRE CENTRAL AND WESTERN DEEP PORTIONS OF THE HARBOUR WERE STRONGLY RELATED. OTHER STRONG RELATIONS WERE FOUND BETWEEN SAMPLES COLLECTED FROM SHALLOW AREAS OF THE NORTH SHORE, AND SILTY AREAS OF THE EASTERN AND NORTHEASTERN PARTS OF THE HARBOUR SUBJECT TO INFLUENCE BY LAKE ONTARIO. AREAS ADJACENT TO INDUSTRIAL AND MUNICIPAL DISCHARGES PRESENT UNIQUE FACTORS AND ARE STRONGLY INFLUENCED BY THESE DISCHARGES. THIS INDICATES THAT IN ORDER TO REDUCE HEAVY METAL CONCENTRATIONS THROUGHOUT MOST OF THE HARBOUR, A LONG PERIOD OF NATURAL SEDIMENT DEPOSITION OR A MASSIVE DREDGING PROGRAM WOULD BE REQUIRED.

SEDIMENT CHEMISTRY

Much of the pollutants discharged to nearshore waters by industries and sewage treatment plants becomes incorporated in bottom sediments by chemical precipitation or absorption, or biological uptake and sedimentation mechanisms. Elements such as iron, manganese and phosphorus in the superficial layers of bottom sediments may exchange with, and become dissolved in hypolimnetic waters under conditions of oxygen depletion (Mortimer, 1941). Organic substances deposited in the sediments are an important source of biological and chemical oxygen demand contributing to deoxygenation of hypolimnetic waters during summer stratification. In addition, the bottom fauna play an important role in the natural ecosystem, and disruption of the bottom fauna by pollution is bound to have a profound effect on the ecosystem. Bottom sediments are thus an important phase of consideration in any detailed water quality study. Therefore, one of the recommendations of the Hamilton Harbour Study 1974 (MOE, 1975) was that further sediment analysis should be undertaken to identify sources of contamination.

A previous study concerning the bottom sediments of Hamilton Harbour was performed in 1964 (Johnson, 1966) as part of a biological survey. Whereas the sediments of most of the bay consisted of silt and clay deposits, an area near the canal indicated fine sands. Iron and phosphorous contents, as well as loss on ignition, were highest in the Ottawa St. slip area and deepest parts and lowest along the northshore. In 1972, the Ontario Ministry of the Environment collected sediment samples from 11 locations in Hamilton Harbour and analyzed them for cadmium, chromium, iron, lead, mercury, and PCB. These results (MOE, 1974) showed high concentrations of heavy metals, especially near Randle's Reef and the Hamilton Sewage Treatment Plant outfall (Figure 1). However, no samples were collected in the deepest central portion of the harbour.

More recently, a statistical technique known as ratio matching has been refined and applied to the Hamilton Harbour data (MOE, 1975). In this method, the ratios of trace pollutant concentrations in pairs of sediment samples are compared, and the results expressed in terms of a matrix of similarity coefficients (Z) which are defined on a scale from 0 to 1, where 0 represents complete dissimilarity and 1 represents complete similarity. This method has the advantage that the effect of dilution of contaminants by inert materials is cancelled by the calculation of ratios of pollutant concentrations, and the coefficients obtained represent a more positive measure of generic similarity between related sediment samples. Mathematical details of the method have already been described (MOE, 1975), and are repeated in Appendix 1.

Field Studies

As part of the 1975 Hamilton Harbour Study, three series of sediment samples were collected. In May, an Ekman dredge was used to collect samples from 20 locations in the harbour, including one at the Lake Ontario end of the ship canal. In June and August, approximately 60 samples were taken from 21 bay locations (Figure 1) with a Phleger corer; these samples were sectioned for analysis when distinct layers were present. All samples were analyzed for aluminum, chromium, copper, nickel, zinc, lead, cadmium, manganese, iron, calcium, magnesium, mercury, cobalt, molybdenum, chemical oxygen demand, biological oxygen demand, loss on ignition, total Kjeldahl nitrogen, total phosphorus, and acid extractable phosphorus. Ten dredged samples were also obtained from Cootes Paradise and Desjardins Canal during June 1975 (See Figure 1).

Results

All core samples collected in June and August were examined prior to analysis, and if discrete layers were evident, these were sectioned and analyzed separately. Visual descriptions of the samples so obtained are given in Table 1. Throughout most of the harbour, surface sediments consist of dark brown or grey to black organic muds, with the blackest muds being obtained along the industrial shoreline or in the deep central area. Brown silts were obtained in the northern part of the harbour along the north shore to Station 257, with light brown sand being found near the ship canal at Station 269. Silt was also found in one sampling of Station 264 at the extreme western end of the harbour. This is similar to the silty clay sediments occurring in adjacent Cootes Paradise.

Mineralogical analysis of the less than 2 micron size fraction of a sediment sample collected by Mudroch (1974) located between Stations 4 and 256 revealed the following composition:

- 37% - illite
- 35% - quartz
- 8% - dolomite
- 6% - chlorite
- 6% - mixed layer (1.0-1.4 nm)
- 3% - K - feldspar
- 3% - plagioclase
- 1% - kaolinite
- 1% - vermiculite

This is comparable to the mineral content of Lake Ontario sediments for which Thomas et al (1972) reported that quartz and clays were the major constituents, averaging 50.8% and 42.3% respectively. The average clay mineral (i.e. less than 2 micron size) content was determined to be 66% illite, 18% chlorite and 15% kaolinite.

Harbour-wide means and standard deviations of all chemical parameters are given in Table 2, sub-divided into top and bottom portions of June and August cores. Chemical analyses of all individual sediment samples obtained in 1975 are given in Appendix II.

NUTRIENTS

Phosphorus

Both total phosphorus and acid-extractable phosphorus were analyzed on all sediments and revealed mean concentrations of 2.3 mg/g and 1.7 mg/g dry weight respectively. The relatively low percentage of organic P recorded in Hamilton Harbour sediments (Mudroch, personal communication) and the high percentage of acid-extractable P would suggest that the concentration of sediment phosphorus is largely controlled by sorption/desorption processes. This is reasonable in view of the elevated iron concentrations observed in the harbour sediments and the documented association of sediment inorganic phosphorus with hydrated iron oxides (Williams et al, 1971; Bortleson and Lee, 1974). The distribution of sediment total phosphorus in May is presented in Figure 2. High phosphorus concentrations were observed in the deep central basin and in the deep hole (Station 4) at the southeastern end of the harbour. In addition to the association of high phosphorus content with the fine particle size of deep-water sediments, sediment phosphorus appears to reflect the discharge of municipal/industrial waste from the Hamilton Sewage Treatment Plant. A sediment sample collected downstream of this effluent in the Windermere Basin was analyzed to contain 12.0 mg/g dry weight phosphorus.

Data from sediment cores further document the high input of phosphorus to the Harbour system in "recent" years. Nitrogen/phosphorus atomic ratios from the top and bottom of six sediment cores of similar length are provided in the following table:

N/P ATOMIC RATIOS IN SEDIMENT CORES, 1975

June Stations	Mudroch (1974)	252	269	20	15	253	37 surface samples
Top	1.18	1.30	2.0	3.8	1.90	1.21	2.40
Bottom	4.15	2.72	3.3	22.7	4.31	1.66	-
August stations		4	20	268	259		
Top		1.48	2.0	2.2	1.48		
Bottom		0.74	2.8	7.5	2.21		

Although results are not consistent, the ratio tends to decrease as one moves up through the core. This decrease is presumed to result from two factors:

1. The upward migration of soluble phosphate ions from the reduced zones of deep sediment.
2. An increased loading of phosphorus to the overlying waters.

The latter feature is probably more significant and is best evidenced at Station 20 in June and Station 268 in August where the discharge of phosphorus from the Hamilton STP has resulted in a 3 to 6-fold decrease in the N/P ratio from the bottom to the top of the sediment core. Inconsistencies in the observed results may be partly due to variable core lengths; as separate samples are to be taken from the top 5 cm in 1976, this effect should be removed.

Sediment Nitrogen

The average concentration of total Kjeldahl nitrogen in 20 surface sediment samples collected from Hamilton Harbour in May, 1975 was 3.6 mg/g (0.36%) dry weight. This is at the lower end of the range of values of 0.1 to 4.0% N defined by Keeney (1973) for lake sediments in general and comparable to the total nitrogen values for Great Lake sediments as shown in the following table:

NITROGEN IN GREAT LAKE SEDIMENTS (from Kemp, 1971)

<u>Station</u>	TOTAL N (% dry wt.)
Lake Huron basin muds	0.39
sands & silts	0.16
Lake Erie basin muds	0.33
sands & silts	0.16
Lake Ontario basin muds	0.43
sands & silts	0.11

In June and August, mud samples were generally 0.2 to 0.3% dry weight total nitrogen, while silt and sand samples were below 0.2%. Thus the relationship to sediment type is similar to that found by Kemp (1971).

Extending the comparison with Lake Ontario sediments, Kemp and Mudrochova (1972) determined that organic nitrogen formed 90 to 95% of the total nitrogen in a bottom sample from Lake Ontario. This organic N was essentially amino acid-N, hexosamine-N, and unidentifiable hydrolysable-N compound. The remaining inorganic nitrogen was primarily ammonium-N, either fixed within clay mineral lattices or in an exchangeable fraction, with nitrate and nitrite being of less importance.

The direct correlation between L.O.I. and total kjeldahl nitrogen, as indicated in Figure 3, shows that a positive correlation exists between total kjeldahl nitrogen and organic matter, since the organic matter but not inorganic carbonates are decomposed by the ignition temperature (600°C) used.

The spatial distribution of sediment total Kjeldahl N recorded in Figure 4 parallels the distribution of sediment phosphorus with depth and emphasizes the importance of size sorting with depth on the concentration of fine-grained sediment components. In addition, the effects of the discharge from the Hamilton Sewage Treatment Plant are indicated in the elevated sediment N concentrations in the extreme southeast corner of the Harbour. In the Windermere Basin, total Kjeldahl N ranged as high as 8.5 mg/g dry weight N.

Heavy Metals

In Table 2, the mean concentrations of heavy metals in Hamilton Harbour sediments are compared to values characteristic of "elevated" and "excessive" heavy metal concentrations in Great Lakes sediments (Fitchko and Hutchinson, 1975). These authors analyzed sediment samples collected from 25 river mouth areas which are representative of non-contaminated areas. These were tributaries with no known industrial or mining activity, and a population of less than 1,000 in the vicinity. To account for natural variability in these outlets they assumed that two standard deviations above the mean accounts for 95% of the natural variability, and thus samples above this limit were considered to contain "elevated" heavy metal concentrations. As an indicator of "gross" contamination, five times this limit was selected as indicating "excessive" concentrations. Table 2 indicates the presence of elevated or excessive concentrations of all these metals but cobalt in Hamilton Harbour; the most excessive concentrations are seen in the case of zinc, chromium and lead.

Figures 5 to 12 indicate the spatial distribution of elevated and excessive heavy metal concentrations according to the average of the surface portions of all samples taken in June and August, except for Station 255, where the June sample was rejected as being anomalously low. Zinc and chromium present almost identical patterns of excessive concentrations everywhere but in the northeast and far western portions, with lead being excessive throughout most of this area. Copper, nickel, manganese and cadmium have elevated concentrations throughout most of the harbour, being excessive only in the areas adjacent to some of the discharges. Concentrations in the northeastern zone and part of the north shore are within the normal range for these metals. Mercury occupies an intermediate position (Figure 12). Excessive concentrations are seen at the Ottawa St. slip, Randle's Reef and part of the deep zone, and elevated concentrations occur elsewhere except in the northeast corner and the farthest west end.

Comparison may be made with other Great Lakes areas (river mouths and harbours) (Fitchko and Hutchinson, 1975; Walters, Wolery and Myser, 1974). Hamilton Harbour sediments are found to have far higher values for iron, zinc and manganese than any other Great Lakes area studied by those authors. These metals are undoubtedly derived from the steel industries. Winchester and Nifong (1971, cited by Fitchko and Hutchinson, 1975) report that zinc and manganese are among the major emissions from these industries. Lead values are higher in Hamilton Harbour than elsewhere in the Great Lakes basin except for Cheboygan River, Lake Huron. Chromium and cadmium values are higher than at most river mouths, although a number of fairly industrialized U. S. areas have higher concentrations of the metals. Copper, nickel and cobalt values in Hamilton Harbour are similar to the industrialized areas along the lower Great Lakes, while mercury values are considerably lower than the contaminated areas of St. Clair River, western Lake Erie and Thunder Bay, which have been affected by the chlor-alkali (St. Clair River, Lake Erie) and pulp and paper (Thunder Bay) industries. In general, Hamilton Harbour sediments are badly contaminated with most heavy metals.

Ranges of classification of Great Lakes sediments into non-polluted, moderately and heavily polluted have been suggested. These classifications are as follows (all figures in $\mu\text{g/g}$):

	<u>Nonpolluted</u>	<u>Moderately Polluted</u>	<u>Heavily Polluted</u>
COD	<40,000	40,000-80,000	>80,000
TKN	<1000	1000-2000	>2000
Pb	<40	40-60	>60
Zn	<90	90-200	>200
Hg	<1.0	-	>1.0
P	<420	420-650	>650
Fe	<17,000	17,000-25,000	>25,000
Ni	<20	20-50	>50
Mn	<300	300-500	>500
Cr	<25	25-75	>75
Cu	<25	25-50	>50

According to June and August data, Hamilton Harbour surface sediments are heavily polluted with respect to COD, Pb, Zn, P, Fe, and Mn and moderately to heavily polluted with respect to TKN, Cr and Cu. The sediments are generally moderately polluted with respect to Ni and nonpolluted with respect to Hg, except in the Ottawa St. slip (heavy Ni and Hg pollution), Randle's Reef (heavy Hg pollution), and Windermere Basin (heavy Ni pollution). Lesser degrees of pollution occur along the northern and northeastern shores and in the far west end.

Available data on the quantity of heavy metal loadings to the harbour (Table 3) reveal substantial inputs of iron, zinc and chromium. The largest variability occurs with chromium, zinc, lead and iron. These metals also represent the largest enrichment in the surface core layers compared to

lower layers. Average surface: bottom ratios were greater than two in all metals but cobalt, and three to six for the above-mentioned metals. Large enrichments of heavy metals in surficial sediments of polluted Great Lakes areas is a common occurrence (e.g. for Lake Erie see Walters, Wolery and Myser, 1974); however, a detailed examination of the chemical stratigraphy of Hamilton Harbour sediments was beyond the scope of this study.

Heavy metal and nutrient concentrations in the May dredge samples tended to be greater than those observed in June and August surface core values by factors of 1.5 to 2 in most parameters, and up to six in the case of mercury. The effect tended to be greater for parameters exhibiting a high ratio of surface to bottom values in core samples. However, sub-samples of dredge samples apparently containing material closest to the sediment-water interface were collected for analysis (R. Semkin, personal communication). These presumably represent the most recently discharged (and therefore most highly enriched) portion of the water column; however the nature of a dredge sample leaves this supposition open to question. In addition, very pronounced enrichment of many heavy metals was observed in a Benthos core sample taken by Mudrochova (1974) from a point near Station 256. Comparing core sections at 0-3 and 15-20 centimeter depth, enrichment of all metals except manganese was observed to a factor of 2 to 100 in the upper portion. As the top portions of cores extracted at Station 256 ranged from 20 to 66 centimeters in length, they comprised both the upper and lower parts of Mudrochova's sample. This emphasizes the extent of recent sedimentation of contaminated materials. For this reason, it is suggested that the top five to seven centimeters of each core collected in 1976 be treated as a separate sample regardless of the presence, absence or location of any color change.

Most mean values in June and August (Table 2) were similar to each other. Significant exceptions were chromium, which was higher in August in both top and bottom portions, and cobalt which was higher in June. However, no significant conclusion can be drawn from this result due to the large variability observed with these parameters (note values of standard deviations in Table 2), as well as the exact location of core sectioning. In addition, local variability is very large (see discussion to follow).

The magnitude of local variability of sediment composition in 1975 samples was examined briefly at five locations representing points near the industrial discharges as well as the deep central basin of the harbour. Results are given in Table 4, along with similarity coefficients derived from the various samples taken in June and August. Considerable variability is seen at stations nearest the industrial and municipal discharges, especially Station 259, where the low observed similarity coefficients (as calculated by the method described in the next section) obtained in June combined with different observed nature of the sediments (see Table 1) dictated separate treatment of one June sample in subsequent analyses. Local variability of the remaining

samples is undoubtedly related to the large extent of enrichment already noted in the surface portion of the sediment cores. The smallest local variability occurred at Stations 258 (deep central part) and 262 (Randle's Reef), despite the observed surface enrichments found at the latter location.

Modification of Ratio Matching Method

In the 1975 Hamilton Harbour report, the significance of the similarity coefficients was established by using a Z-test for significant difference from 0, and random numbers from uniform and log normal distributions were analyzed to verify the sensitivity of the test. The procedure yielded reasonable results for 6 to 8 chemical parameters; however, it was not tested for more than 8 parameters. When the May 1975 data were analysed using 16 chemical parameters, 99 percent of the similarity coefficients were significant at the 95 percent confidence level, with several of the coefficients exceeding the 99.99 percent level. As this result was not credible a random data set consisting of uniformly distributed numbers from 0 to 1 was prepared and analyzed for 16 parameters. Approximately 50 percent of the similarity coefficients exceeded the 95 percent confidence level as opposed to 1 to 5 percent of the coefficients derived from similar random data sets containing six to eight parameters. It was therefore decided to modify the procedure of establishing statistical significance.

If it is considered that the similarity of samples arises due to non-randomness of the data, a measure of similarity would be the deviation of the real similarity coefficients from a set of similarity coefficients computed from random data of similar characteristics to the real data. Assuming that the data for each chemical parameter is approximately log normally distributed, the mean and standard deviation of the logarithms of the data for each parameter are calculated, and random data with log normal distribution are generated for at least 20 sampling stations for each parameter. These random data sets are processed to find a set of similarity coefficients, and the mean and standard deviation of these coefficients are obtained. The 95 percent confidence limit L of the random similarity coefficients is given by:

$$L = \mu + \sigma(t_{0.05, n-1}) \quad (1)$$

where

- μ = mean of transformed similarity coefficients
- σ = standard deviation of transformed similarity coefficients
- n = number of chemical parameters.

In order to avoid the value of L exceeding the maximum possible value of 1.0, an additional transformation is performed in the similarity coefficient matrix, as follows:

$$Z_t(kl) = -\log_{10} \{1 - Z(kl)\} \quad (2)$$

where: k and l are sampling stations, and Z is the similarity coefficient as previously described.

The computation of the similarity coefficient Z from the previous Hamilton Harbour study is repeated in Appendix I for reference purposes.

The test for significant matches (i.e. similarity coefficients significantly different from zero) is merely:

$$Z_t(kl) > L \quad (3)$$

As the results of the generation of random data from the means and standard deviations of the logarithms of real data are dependent on the seed, or initial value, input to the random number generator, the process of generating random data sets is repeated until two random data sets are obtained which yield limiting similarity coefficient values which agree within 0.5 percent of each other.

This method was tested by analyzing random data generated from normal, uniform, and log normal distributions. Results obtained from these data sets are summarized in Table 5. A comparison of the value of the limiting similarity coefficient obtained by the above procedure with the mean and standard deviation of results obtained from 10 random data sets indicates that this procedure will usually yield a number that is within 1 standard deviation of that obtained by averaging the results of 10 random data sets. In addition, this method obtains a reasonably small number of significant matches for any type of input random data regardless of the distribution used. This overcomes the problem that was observed previously with normally distributed data sets with relatively small variance which yielded up to 100 percent significant similarity coefficients. This result was noted in the 1975 Hamilton Harbour report, but was thought to be due to similarity of samples. With the new method of calculating log normally distributed data sets for each parameter under study, the random nature of these data sets is borne out, even for analysis with up to 24 parameters.

Although the use of log normally distributed random data sets in the significance calculation may appear to be somewhat arbitrary, it does provide a means to differentiate between real and random variations in input data. Log normal distributions are preferred to normal distributions as the latter could produce negative random numbers from chemical data in which the standard deviation is comparable to the mean, as is frequently true.

The present computer program uses the Kolmogorov-Smirnov test to estimate the probability of normal and log normal distributions for each chemical parameter. Although test results frequently indicate a higher probability of normal distribution than of log normal distributions, log normal distribution is preferred for the reason already stated.

Factor Analysis of Similarity Coefficients

As the ratio matching method did not have the desired sensitivity to indicate spatial correlations when applied to large sets of data, factor analysis was performed on the similarity coefficients. Factor analysis (Harbaugh and

Merriam, 1968) is basically a procedure for simplifying a large number of measurements in terms of a few definite patterns, or factors. It was originally developed by social scientists; however, the techniques have also been applied to such diverse fields as biology, business and geology.

Factor analysis is used to study either relationships between observations (in this case samples) called the Q - mode or between variables (in this case chemical parameters) called R - mode. Given some type of correlation matrix, new variables are constructed in geometric space, which are orthogonal to each other, and thus independent of each other. Although a graphical analogy to this procedure may be drawn in three-dimensions (Harbaugh and Merriam, 1968), the procedure may be extended to any number of orthogonal dimensions. In such space, each variable (or observation) may be represented as a vector; closely correlated variables will be clustered together, while uncorrelated variables will be at right angles to each other. The normalized component of each vector along each factor axis is called the factor loading of the variable; therefore this is a measure of the degree to which a given factor is descriptive of any variable. In order to simplify these relationships, the factor axes are rotated so that each axis is most descriptive of a group of highly related variables, i.e. loadings near 1.0 or -1.0. Thus groups of highly related variables (or observations) may be identified by their factor loadings.

In this work, factor analysis is applied in the Q - mode to the similarity coefficient matrix calculated by the method given in Appendix I, and also in the R - mode to ordinary correlation coefficients between chemical parameters.

Ratio Matching and Factor Analysis

For further assessment of pollutant distributions and the manner in which they are affected by the various discharges, the improved concentration ratio matching method as described in this section was applied to the 1975 sediment data. Table 6 presents the similarity coefficients derived from the May 1975 dredge samples. A large number of highly significant relationships (coefficients of about 0.75) are seen, involving combinations of deep water stations throughout nearly the entire harbour. However, as the 95 and 99 percent limiting values derived by the method presented earlier are 0.592 and 0.621, the results indicate that nearly all the possible combinations are statistically significant, as might be suspected in a relatively confined water body subject to numerous industrial and municipal discharges. The situation is even more severe when the top portions only of the June and August data sets are considered, even when the values of highly similar samples taken from the same location are averaged. As is seen in Table 7, 37 to 64 percent of the average similarity coefficients, consisting of sets of 210 to 561 coefficients are significant at the 99 percent level.

Even at a reduced number of chemical parameters (9, when Cootes Paradise data are included), a formidable number of significant matches occurs. It was decided to use factor analysis on the similarity coefficients to separate these relationships into groups defining areas of related sediment characteristics.

With these facts in mind, Q mode factor analysis was conducted on the similarity coefficient matrices derived from the May, June and August sediment samples. Eigenvalues were permitted to drop to a sufficiently low value as to obtain a resolution of the data into enough factors to permit a delineation of the zones of generically related sediments. All chemical parameters that were employed in the similarity analysis were used for factor analysis. In addition, the June Hamilton Harbour data were combined with a series of samples taken from Cootes Paradise and Desjardins Canal during June 1975. These ratios were analyzed using a subset of nine chemical parameters common to all samples (Cu, Zn, Pb, Cd, Mn, Fe, LOI, total P, TKN). Results are shown in Figures 13 to 16.

The most dominant grouping in all analyses consists of the entire western and central deep portions of the harbour, including samples obtained from the western portion of the north shore and some offshore portions of the eastern part of the industrial shoreline. The eastward extent of this group varied with the data set being considered, reaching Station 254 in May, Stations 4, 256 and 257 in June, and Station 255 (but not 254) in August. In further discussions this factor will be referred to as the principal factor.

Also common to all analyses was the fact that stations most affected by industrial and municipal discharges tended to belong to unique factors. Such stations were: 268 (near Windermere Basin), 2 (in the Ottawa Street slip) and 264 at the far west end of the harbour near the Cootes Paradise entrance). Station 262 (Randle's Reef) presented a unique factor in the August data, but belonged to the principal factor in the May and June analyses. In June, analysis to a lower eigenvalue did produce a unique factor for Station 262, however.

A grouping in the southeastern portion of the harbour indicated a zone subjected to the combined effect of the municipal discharge as well as the steel plant discharges. In May, this grouping was of Stations 20, 4, 256 and 255 indicating that the industrial discharges affected the deep eastern hole and tended to spread towards the central part of the harbour. Except for Station 255 (whose characteristic is variable, as seen below), this zone corresponds roughly to the predicted area of most contaminated water as depicted by the numerical model (MOE, 1974, Section E). In June, this area consisted solely of Station 20, although one of the three samples collected at Station 256 presented another unique factor at low eigenvalues.

In August, two separate factors were observed: Stations 20 and 267, along the far eastern shore of the harbour; and Stations 256, 4 and 254, extending from the mouth of the Ottawa Street slip to the deep eastern hole and the eastern portion of the main deep area. The former factor lies within a zone of oscillatory currents of mixed directions (MOE, 1974, Section E) producing conditions suitable for precipitation of components such as organic complexes or finely divided (and hence suspended) particulates. The presence of Station 254 in this factor rather than the principal factor is rather puzzling, however. Similarity coefficients indicate this station to be similar in nature to both groupings.

Other predominant factor groupings occupied the northern and northeastern portions of the harbour. In May, Stations 269 and 1030 on the opposite ends of the ship canal were strongly related, as might be expected considering the extent of lake-harbour exchange. These stations were also related to Station 264 at the far west end of the bay. This fact is probably related to the presence of silty materials at Station 264 (see Table 1). In June, Stations 252, 269, 255 and one sample of 259 were related. This grouping represents the area of silty sands and provides a rough definition of areas subject to influence by Lake Ontario, in agreement with previous findings (Johnson, 1964). The fact that one sample of Station 259 is related to this group and two samples were related to the principal factor indicates the variable nature of sediments which may be found within a few meters of each other, in an area in which varied mixing processes and bottom scour due to natural currents may expose different types of sediments. This fact was also reflected in the depths of the similar upper portions of the cores collected in June and August at this location, which varied from 3 to 60 cm.

Station 255 also represents a zone of conflict between the different transport processes, as it was located in the southeastern factor in May, the northeastern factor in June and the principal factor during August. Difficulty in exact replication of sampling vessel positioning during repeat surveys may play a role in this difference.

Finally, several factors were found relating north shore sediment locations. In May, Stations 252 and 257 were related, as also were 253 and 260, though Station 253 was also partially related to the principal factor. These relationships probably reflect varied water depths with the deeper sediments being exposed to anoxic hypolimnetic water during a greater portion of the time. As depth measurements were not made, however, this cannot be proven; in 1976 it is suggested that depth measurements be made at the point of all core samples.

In August, two factors were found for Stations 252 and 257 respectively; lack of samples from Stations 253 and 269 prevented good definition of the various relationships in this part of the harbour for this time period.

Relationship to Cootes Paradise Sediments

Additional interesting relationships were obtained when the June data were combined with data obtained in Cootes Paradise, as shown in Figure 15. Within the main part of the harbour, results were similar to those obtained previously, except that the north shore factors were not visible. Several interesting relationships between Hamilton Harbour and Cootes Paradise were found. For example, a relationship was observed between Station 268 (nearest the Hamilton STP) and samples collected close to the Dundas STP outfall. In addition, samples collected from the western portion of Cootes Paradise and Desjardines Canal relate to Station 20. This shows the obvious effect of materials from the sewage plants that are not immediately deposited, or are incorporated into biological growth which is later sedimented a short distance from the outfall. Finally, exchange through the channel between Hamilton Harbour and Cootes Paradise has produced a similar sediment environment at the neighbouring locations 264 and CP-1, reflecting the existence of a significant exchange between the two water bodies. During 1976, a current meter mooring is to be undertaken in order to further study this exchange.

One sample near the entrance to Desjardins Canal was also partly related to the samples at the eastern end of the harbour. In fact, the entire series of samples from this part of Cootes Paradise can be related to the east end of the harbour if the analysis is stopped at a higher eigenvalue. This could be due to the fact that the sediments of both areas are silty sands despite the more highly polluted levels of the Cootes sediments with respect to copper, zinc, lead, manganese and LOI.

R-Mode Factor Analysis

In order to assess which elements behaved similarly during sedimentation, R-mode factor analysis was performed on the correlation matrices of the June and August data sets. The results are given in Tables 8 and 9, respectively. These results express the relationship between the concentrations of the various pollutants in terms of factors which are linear combinations of the variables, for example (factor 1, Table 8):

$$\begin{aligned}\text{Factor 1} = & 0.927 \text{ Cr} + 0.893 \text{ Cu} + 0.924 \text{ Ni} + \\ & 0.630 \text{ Mn} + 0.543 \text{ Fe} + 0.490 \text{ Hg} + \\ & 0.782 \text{ Co} + 0.634 \text{ COD} + 0.422 \text{ LOI}\end{aligned}$$

In both cases, transition metals such as Cr, Cu, Ni, Fe and Co are all associated in one factor while post-transition metals (Zn, Pb, Cd, Hg) are associated in a separate factor, although Mn is associated with both factors and in June Fe is also associated with a unique factor. The fact that both groups of metals are related to organics is indicated by their associations with COD and LOI in both months.

Discussion

Factor analysis of the similarity coefficients obtained by the ratio matching method facilitates a division of Hamilton Harbour into areas in which similar transport mechanisms are operative despite varied absolute concentrations, and, in particular, a tendency for the concentrations of most parameters to increase toward the deepest parts of the harbour. The fact that the sediments of most of the deep portion of the harbour are related in the principal factor indicates that common transport mechanisms are important in moving pollutants away from nearshore zones characteristic of the nearby discharges.

Numerous studies have been performed on the mechanisms of pollutant transport in the sediments of rivers, lakes and estuaries. For example, Pita and Hyne (1975) found that Zn and Pb are associated with clay particles in reservoirs, with their concentrations increasing towards the deepest portion of the reservoirs. Zn was found to be more mobile than Pb. Schindler et al (1972) found that organic materials of large molecular weight can associate Fe, Mn and Mg while Zn was associated with a lower molecular weight fraction. They concluded that organics play an important role in the movement and re-solution of sedimented metals during stratification. In a study of trace metals in the Amazon and Yukon rivers, Gibbs (1973) found that transport in precipitated and coprecipitated solids and crystalline sediments were the predominant modes of transport for Fe, Ni, Co, Cr, Cu and Mn. Only Cr and Mn were transported to a significant (>10%) extent in solution. In a Maryland estuary study, Helz, Huggett and Hill (1975) found that transport processes such as adsorption, precipitation, colloidal flocculation or biological uptake were important in removing Zn, Cu, Pb and Cd from the water near a sewage outfall. Cation exchange and decay of organic complexes also facilitated selective transport of Cd seaward as opposed to Zn. Cation exchange processes were also believed to be important in the transport of Cd and Ni from sediments contaminated by discharge from a battery plant (Bondietti et al 1973). Certainly, similar processes are important in trace-metal transport with Hamilton Harbour sediments.

Factor analysis between parameters (R-mode) (Tables 8 and 9) indicated a division of the metals into two factors: transition metals in which electrons occupy only a portion of the outer d-orbitals (Cr, Mn, Fe, Co, Ni and Cu); and post-transition metals in which these orbitals are completely filled (Zn, Cd, Hg and Pb). As crystal-field stabilization theory (Cotton and Wilkinson, 1972) predicts that the former group will tend to form more stable complexes than the latter, complex formation and transport from the harbour may be more significant for the transition metals as opposed to the post-transition group, which is slowly transported as adsorbed or crystalline solids to the deeper part of the harbour. Manganese, which contains a half-filled

outer d-shell, is stabilized only by ligands which possess a strong crystal-field effect. Thus its appearance in both factors is plausible. Comparison of sediment metal concentrations in relatively unpolluted shallow locations to those in nearby deep areas (Table 10) lends some credibility to this supposition, as the post-transition metals tend to be relatively more concentrated in the deep zones compared to the transition metals. However, other factors (biological, geological) will also play a role in the sediment transport. Association with organic materials is definitely important with respect to both types of metals (Schindler et al, 1972), in solids as well as in solution (Gibbs, 1973).

Since the heavy metals tend to be transported toward the deep portions of the harbour, the highest concentrations of pollutants in the shallow zones may be used to indicate problem areas (Table 11). The problem areas are Randles Reef (Mn, Fe, Zn, Cd, Hg, Pb), Ottawa Street slip (all metals) and the Hamilton Sewage Treatment Plant (Ni, Cu, Cr). With regard to Randles Reef, Fe and Zn loadings from Stelco are documented (Table 3). Industrial waste analyses have not been done for the other metals; thus, their source is unknown.

Because of the existing transport processes, it must be concluded that reduction or elimination of heavy metal loading would have a significant effect only in the sediments immediately adjacent to the outfalls; if it were needed to reduce heavy metals concentrations elsewhere, a long period of natural sediment deposition or a massive dredging program would be required.

Limitations of the Ratio Matching Technique

It must be emphasized that the entire ratio matching and factor analysis method is based on drawing logical deductions from statistical manipulations of analytical data. Variability in results can come from any of the following:

- a. Analytical precision.
- b. Spatial variation, for example, horizontal variation as a result of boat movement between collection of replicate cores, or difficulty in obtaining the same position on two separate cruises, or vertical variability, as was seen from the highly stratified results evident in some core samples (Table 2).
- c. Temporal variability, changes with time of sediment chemistry should not be great, however, seasonal variation could occur as a result of leaching or precipitation of ions in the sediment as has been seen in some laboratory studies, for example Mortimer (1971).

The variability in terms of multiple samples collected from the same location was examined in the 1975 data by processing a sub-set consisting of the three samples collected at Stations 252, 20, 258 and 259 in June and August. Of these stations, 258 and 259 are related; 20 and 252 are independent of each other and the first two stations. Factor analysis results for these samples are given in Table 12 for June data and Table 13 for August data. Table 12 illustrates the difference observed in sample 259C with respect to the other samples obtained at Stations 258 and 259. It was for this reason that sample 259C was considered as a separate station in the earlier treatment of the June results. Table 12 indicates how this sample is associated with both the principal factor (258, 259) and Station 252. The variability observed at Station 20 is also illustrated in the variable factor loadings which occurred for factor three with this station. In August, the analyses for Station 252 were highly variable, while Stations 258, 259 and 20 yielded samples very similar to each other. The latter fact was noted previously (Table 4). Factor analysis divides the results for Station 252 into two factors, with factor three (sample 252C) being weakly associated with Station 259. As expected, Stations 258 and 259 were well associated (factor four) while Station 20 was independent (factor one). These results clearly indicate the limitations of this method when applied to large sets of sediment data.

It should be possible to save analytical costs by only doing one or two parameters from each factor obtained by the R-mode factor analysis, as such factors include chemical parameters which are closely related. Such a sub-set should contain a fewer, but still reasonable, number of similarity coefficients which are significant at the 95 or 99% confidence level, and factor analysis should yield similar factor loadings to those obtained with the full set. On the other hand, concentrating on all parameters from one or two factors of the R-mode analysis should suggest how these parameters are transported in particular, as effects of other parameters have then been eliminated. The exact analyses to be done should depend upon the desired applications of the method.

For 1976, a few changes can be suggested in the sediment sampling program. First, more locations should be sampled near the industrial shoreline. To take account of the observed spatial variabilities, it is suggested that two samples per location per cruise be taken. As most of the central and west-central parts of the harbour are strongly interrelated, fewer samples are needed from this area, and only one sample per location. Along the north shore it is suggested that two samples per station be taken but from slightly different locations, one from a shallow point where the water depth is less than 6 meters and thus not exposed to anoxic hypolimnetic conditions and another sample from a deeper water depth, i.e. greater than 10 meters. Fractionation of sediment particle sizes between depths may also be important in this regard. It should not be necessary to

analyze for many parameters, and in particular parameters can be selected from the R-mode factor loading (Table 8 and 9), and the depth stratification within the cores (Table 2). The top five centimeters of each core should be considered a separate sample regardless of the appearance of the core. In addition, it would be interesting to obtain analyses of the suspended solids from the principal industrial outfalls and include these results in the similarity matrices. This should allow for better identification of the zones of contamination and the sources of such contamination.

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TABLE 1

DESCRIPTION OF JUNE AND AUGUST 1975 CORE SAMPLES

<u>Station</u>	<u>June</u>		<u>August</u>	
	<u>Top</u>	<u>Bottom</u>	<u>Top</u>	<u>Bottom</u>
252	brown sandy silt	light brown sand	brown silt	-
269	3-7 cm light brown sand	dark brown organic	-	-
267	dark brown organic	-	dark brown organic	-
20	3-8 cm dark brown organic	light brown silt	40-60 cm dark brown organic	grey sand
268	dark brown organic	-	8 cm black organic	dark brown organic
256	15-25 cm black organic	dark brown organic	20-65 cm black organic	light grey silt, divided in one of 3 cores into upper (darker) and lower layers
2	black organic	-	black organic	-
4	black organic	-	10 cm black organic	light grey silt
255	5 cm grey silt	brown organic	dark grey silt interspersed with lighter material	-
259	two cores black organic, one core brown silt	-	3-50 cm black organic	light brown silt
262	black organic	-	40 cm black organic	grey silt (in one of 3 cores only)

TABLE 1 (Continued)

<u>Station</u>	<u>June</u>		<u>August</u>	
	<u>Top</u>	<u>Bottom</u>	<u>Top</u>	<u>Bottom</u>
261	dark brown organic (20 cm)	-	black organic	-
15	3-5 cm light brown silt	brown organic	brown organic	-
270	12 cm brown organic	dark brown organic	dark grey - brown organic	-
271	brown organic	-	light brown organic	-
264	12 cm light brown silt	black organic	dark grey - black organic	-
272	45 cm dark brown organic	light brown sandy	dark grey organic	-
258	black organic	-	grey-black organic	-
254	greyish black organic	-	33 cm dark brown organic	light brown silt
253	3 cm light brown silt	dark brown organic	-	-
257	8-17 cm dark brown silt	light brown silt	23 cm dark grey-brown silt	13 cm light brown silt, over organic layer

TABLE 2

MEAN RESULTS OF HAMILTON HARBOUR SEDIMENT ANALYSES, 1975

	May			June			August			Great Lakes Concentration Elevated	Comparative Values Excessive
	Mean	S.D.	Top	Mean	S.D.	Bottom	Mean	S.D.	Bottom		
			Mean			Mean			Mean		
Cu	101	59	66	44	32	35	71	56	34	21	104
Cr	206	150	99	76	25	26	170	260	58	16	82
Ni	45	19	29	15	12	17	33	30	16	28	142
Zn	3110	2000	1540	1720	290	270	1750	1740	230	118	591
Pb	320	200	200	240	46	50	210	200	70	28	140
Cd	7.8	5.1	4.8	3.8	1.7	2.0	3.8	2.4	1.4	2.2	8.5
Mn	1670	920	1100	510	180	740	1260	640	610	453	2265
Fe (mg/g)	68	41	74	136	16	24	61	74	19	6	-
Hg	2.4	2.4	0.4	0.3	0.2	0.2	0.4	0.3	0.1	0.2	0.58
Co	15	4	7.9	3.3	2.4	7.1	3.0	3.6	4.8	1.2	90
COD (mg/g)	152.	87	90	63	28	67	110	68	60	44	-
LOI (%)	10.5	6.2	7.7	3.8	2.8	6.6	7.8	3.1	5.0	3.0	-
TKN (mg/g)	3.5	2.0	2.1	1.2	0.9	1.8	1.6	0.7	1.4	1.1	-
Tot P (mg/g)	3.4	1.7	1.8	0.8	0.6	0.9	1.7	0.4	1.0	0.4	-
Acid Ext. P (mg/g)	2.3	0.9	1.3	0.7	0.4	0.7	1.4	0.3	0.8	0.3	-
As	-	-	-	-	-	-	11.5	7.3	3.8	1.6	-
Sulfide	-	-	-	-	-	-	367	594	24	11	-
Al (mg/g)	-	-	9.6	4.4	4.8	8.2	10.2	6.4	6.0	1.8	-
Ca (mg/g)	-	-	48	15	32	55	*56	25	*98	49	-
Mg (mg/g)	-	-	7.8	2.1	1.4	7.5	*6.0	1.3	*5.7	2.0	-

Note: All analyses are in ppm (ug/g), unless otherwise stated.

"Top" and "Bottom" refer to the top and bottom portions of core samples.

*These metal samples were analyzed by emission spectrograph. All other metals were analyzed by atomic absorption spectrograph.

Great Lakes concentration comparative values are based on (mean + 2S.D.) and 5(mean + 2S.D.) of heavy metal concentrations found in the sediments of 25 relatively undeveloped river-mouth locations (Fitchko and Hutchinson, 1975).

TABLE 3

HEAVY METAL LOADINGS TO HAMILTON HARBOUR: (kg/day)

	Fe	Zn	Cu	Pb	Cr	Ni	Cd	Mn
STELCO ¹	4,500	640	--	--	45	--	--	--
DOFASCO ¹	3,200	45	--	--	23	--	--	--
HAMILTON STP ²	--	40	9.5	8.6	18	18	2.7	20
BURLINGTON STP ³	7.3	4.5	1.1	--	0.7	1.8	--	5.1
ATMOSPHERIC PRECIPITATION ⁴	1.6	6.1	0.4	1.4	--	0.2	0.1	--

1. 1975 Data, MOE, Industrial Abatement
2. 9 samples - 2 from 12 May 75, 1 from 13 May 75, 3 from 19 May 75, 3 from 31 July 75. J. Smart, Wastewater Treatment Section, Pollution Control Branch, MOE.
3. Oliver, B.G. and E.F. Cosgrove. 1975 Metal Concentrations in the Sewage, effluent and sludges of some Southern Ontario wastewater treatment plants. Water and Wastewater Treatment Research, CCIW.
4. Shiomi, M.T. and K.W. Kuntz. 1973 Great Lakes Precipitation Chemistry: Part 1, Lake Ontario Basin. Proc. 16th Conf. Great Lakes Research, p. 581-602.

TABLE 4

VARIATION OBSERVED IN MULTIPLE
SAMPLES OF HAMILTON HARBOUR SEDIMENT

Station 20

	May	June		August	
		Mean	S.D.	Mean	S.D.
Cu	213	35	12	62	9
Ni	53	13	5	21	2
Zn	4030	400	230	1000	180
Pb	478	44	45	123	20
Cd	12	0.7	0.3	2.5	0.6
Mn	1540	870	120	1050	70
Fe (mg/g)	116	17	15	41	5
Hg	7.3	0.11	0.06	0.38	0.02
Co	19	3.0	0.0	5	3
COD (mg/g)	230	70	17	92	11
LOI (%)	16	4.2	1.0	7.0	1.0
TKN (mg/g)	5.8	2.2	0.5	1.7	0.1
P (mg/g)	6.2	1.2	0.4	1.9	0.2
Similarity	A-B	.729		.816	
Coefficients:	A-C	.671		.831	
	B-C	.683		.891	

Note: All analyses are in ppm (ug/g), unless otherwise stated,
Similarity coefficients are between three samples (A, B
and C) collected at the same time.
Top portions of cores only used.

TABLE 4 (Continued)

VARIATION OBSERVED IN MULTIPLE
SAMPLES OF HAMILTON HARBOUR SEDIMENT

Station 256

	May	June		August	
		Mean	S.D.	Mean	S.D.
Cu	144	106	39	97	5
Ni	58	22	16	36	3
Zn	3420	2500	970	3450	1020
Pb	393	300	110	420	190
Cd	6.6	5.4	1.3	6.8	2.5
Mn	2340	770	890	1510	90
Fe (mg/g)	124	84	30	85	3
Hg	3.4	0.43	0.50	0.73	0.18
Co	17	8.2	2.6	8.0	2.0
COD (mg/g)	260	130	60	125	13
LOI (%)	21	9.7	2.5	8.9	0.7
TKN (mg/g)	6.0	3.0	1.0	2.2	0.4
P (mg/g)	3.0	2.4	1.1	2.3	0.1
Similarity	A-B	.750		.790 (.863)	
Coefficients:	A-C	.824		.731 (.835)	
	B-C	.780		.810	

Note: All analyses are in ppm (ug/g), unless otherwise stated. Similarity coefficients are between three samples (A, B and C) collected at the same time. Top portions of cores only used. August core A was sectioned into 3 zones, the center of which was more similar to cores B and C. Similarity coefficients between the center portion of core A and the other cores are indicated in brackets.

TABLE 4 (Continued)

VARIATION OBSERVED IN MULTIPLE
SAMPLES OF HAMILTON HARBOUR SEDIMENT

Station 258

	May	June		August	
		Mean	S.D.	Mean	S.D.
Cu	172	93	15	72	12
Ni	68	40	4	33	2
Zn	6510	1600	150	1030	320
Pb	667	215	22	136	38
Cd	16	7.1	1.8	4.0	1.4
Mn	3070	1450	220	1270	250
Fe (mg/g)	136	68	6	51	9
Hg	6.2	0.70	0.16	0.48	0.12
Co	22	10	2	11	2
COD (mg/g)	255	117	12	102	13
LOI (%)	17	10.8	1.2	10.2	0.7
TKN (mg/g)	5.9	3.1	0.2	2.3	0.4
P (mg/g)	5.3	2.2	0.2	2.0	0.3
Similarity	A-B	.853		.820	
Coefficients:	A-C	.870		.843	
	B-C	.855		.809	

Note: All analyses are in ppm (ug/g), unless otherwise stated.
Similarity coefficients are between three samples (A, B and C) collected at the same time.

TABLE 4 (Continued)

VARIATION OBSERVED IN MULTIPLE
SAMPLES OF HAMILTON HARBOUR SEDIMENT

Station 259

	May	June		August	
		Mean	S. D.	Mean	S.D.
Cu	87	55	36	38	8
Ni	38	30	14	19	4
Zn	3330	1730	1750	920	450
Pb	369	210	180	120	54
Cd	7.2	4	4	2.1	0.9
Mn	2750	1600	760	1240	290
Fe (mg/g)	79.6	53	36	36	8
Hg	0.63	0.3	0.3	0.2	0.1
Co	16	30	35	8.7	0.8
COD (mg/g)	145	110	80	69	12
LOI (%)	7.5	7.6	4.7	5.4	0.4
TKN (mg/g)	3.3	1.6	1.1	0.9	0.3
P (mg/g)	2.7	1.7	1.3	1.2	0.3
Similarity	A-B	.814		.840	
Coefficients:	A-C	.686		.774	
	B-C	.646		.846	

Note: All analyses are in ppm (ug/g), unless otherwise stated.
Similarity coefficients are between three samples (A, B
and C) collected at the same time.

Table 4 (Continued)

VARIATION OBSERVED IN MULTIPLE
SAMPLES OF HAMILTON HARBOUR SEDIMENT

Station 262

	May	June		August	
		Mean	S.D.	Mean	S.D.
Cu	57	105	6	72	16
Ni	28	39	2	28	7
Zn	1950	7800	650	5900	1900
Pb	486	1110	170	670	220
Cd	4.6	11.7	0.6	7.7	2.9
Mn	1270	2200	450	2370	570
Fe (mg/g)	55.8	139	18	115	30
Hg	3.6	1.0	0.4	1.0	0.3
Co	12	9.7	1.3	8.3	0.8
COD (mg/g)	150	288	8	217	62
LOI (%)	8.0	15.7	2.1	11.7	3.8
TKN (mg/g)	1.9	3.9	0.1	1.8	0.3
P (mg/g)	1.3	2.5	0.4	2.0	0.3
Similarity	A-B	.804		.930	
Coefficients:	A-C	.852		.877	
	B-C	.898		.851	

Note: All analyses are in ppm (ug/g), unless otherwise stated.
Similarity coefficients are between three samples (A, B and C) collected at the same time.

TABLE 5

SIMILARITY COEFFICIENTS CALCULATED FROM RANDOM DATA SETS

Characteristic of Data Set	No. of Stn.	No. of Parameters	No. of Matches (Old Method)	Results of New Method			
				Average of 10 Trials		Two Trials within 0.5%	
				Limiting coefficient	# of Matches	Limiting Sim. Coeff.	# of Matches
				Mean	S.D.	Mean	S.D.
Normal, each para- meter had separate mean in range							
0-100	21	8	210	0.8390	0.0150	3	3
						0.8415	2
Normal, mean	21	8	210	0.9460	0.0068	1	1
10, SD 2	20	24	190	0.9055	0.0053	3	2
						0.8982	7
Uniform in range	20	8	0	0.6436	0.0120	1	1
0-100	20	20	136	----	----	-	-
	20	24	190	0.5585	0.0076	15	5
						0.6397	1
						0.5720	8
						0.5652	12
Log-normal,	20	6	0	----	----	-	-
ln mean=1, ln SD=1	20	16	45	0.5855	0.0088	3	0
						0.6421	3
						0.5806	3

Note: 95% limiting level is used in determining significant level of all matches.
 Old Method is as described in MOE, 1975.
 190 (at 20 stations) or 210 (at 21 stations) represent 100% matches.

MAY/75 HAMILTON HARBOUR SEDIMENT SAMPLES

MATRIX OF SIMILARITY COEFFICIENTS

EACH COEFFICIENT IS BASED ON A SCALE FROM 0 TO 1

	252	260	256	4	269	255	254	258	264	260	270	15	261	262	263	257	253	1030	268	259
252	.000	.634	.637	.084	.657	.626	.650	.634	.576	.674	.673	.713	.656	.587	.642	.787	.672	.558	.566	.629
260		.000	.747	.773	.547	.730	.769	.759	.524	.638	.703	.680	.717	.669	.697	.703	.655	.481	.566	.640
256			.000	.767	.596	.710	.730	.733	.525	.624	.007	.672	.694	.682	.671	.704	.625	.504	.594	.658
4				.000	.603	.769	.818	.785	.550	.695	.749	.757	.760	.664	.749	.790	.691	.512	.501	.721
269					.000	.500	.573	.564	.616	.620	.589	.636	.571	.568	.577	.642	.617	.678	.599	.621
255						.000	.788	.771	.617	.742	.704	.720	.740	.651	.709	.708	.717	.550	.603	.736
254							.000	.694	.558	.719	.793	.775	.854	.709	.822	.743	.732	.501	.544	.755
258								.000	.550	.709	.762	.755	.659	.728	.838	.722	.727	.490	.539	.746
264									.000	.624	.573	.614	.559	.554	.569	.586	.600	.621	.508	.592
260										.000	.770	.784	.717	.017	.771	.738	.849	.550	.582	.789
270											.000	.837	.834	.678	.867	.736	.762	.502	.558	.728
15												.000	.796	.672	.821	.787	.780	.542	.549	.753
261													.000	.709	.874	.726	.735	.491	.546	.729
262														.000	.678	.650	.608	.503	.539	.659
263															.000	.713	.789	.500	.536	.758
257																.000	.722	.549	.570	.710
253																	.000	.533	.503	.767
1030																		.000	.545	.540
268																			.000	.564
259																				.000

TABLE 7

PERCENTAGE OF SIGNIFICANT MATCHES
OBTAINED IN HAMILTON HARBOUR BY THE
RATIO MATCHING TECHNIQUE

Data Set	Number of Chemical Parameters	Number of Similarity Coefficients	Percentage of Significant Matches	
			95% Level	99% Level
May	16	190	72.6	65.3
June	14	1596	66.1	53.4
June, with similar samples averaged	14	465	69.0	57.0
June, top portions only, similar samples averaged	14	210	76.2	64.3
June, top portions only, similar samples averaged, plus Cootes Paradise data	9	496	52.2	36.9
August	15	1128	63.4	50.7
August, with similar samples averaged	15	465	61.9	50.8

TABLE 8

R - mode factor analysis of June 1975
Hamilton Harbour sediment samples

VARIABLE	COMMUNALITY	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5
Cr	0.97515	0.9274	-0.1567	-0.2585	-0.0414	0.1481
Cu	0.97454	0.8937	0.1587	0.3717	-0.0616	0.0933
Ni	0.94331	0.9240	0.0209	0.2496	-0.1119	0.1196
Zn	0.96445	0.1861	0.0667	0.9442	-0.0862	0.1625
Pb	0.92925	0.2675	0.0529	0.9080	-0.0929	0.1479
Cd	0.90749	0.1184	0.5035	0.7936	-0.1005	-0.0094
Mn	0.90587	0.6303	0.0376	0.6767	-0.0250	0.2205
Fe	0.97961	0.5431	-0.0898	0.2718	-0.0620	0.7739
Hg	0.85548	0.4902	0.2258	0.7297	-0.1277	0.1244
Co	0.91976	0.7816	0.4500	0.2736	-0.1394	0.1095
COD	0.95059	0.6339	0.0303	0.7317	0.0573	0.0963
LOI	0.81321	0.4216	0.2597	0.7494	0.0633	-0.0494
TKN	0.88390	0.2782	0.5647	0.6591	0.2273	-0.0394
P	0.80979	0.4149	0.5321	0.5701	-0.1677	0.0379
Al	0.95872	0.0770	0.9456	0.1027	-0.2137	-0.0486
Ca	0.97756	-0.1430	-0.1194	-0.0764	0.9673	-0.0364
Mg	0.89558	-0.0910	0.9280	0.1549	0.0454	-0.0117

TABLE 9

R-mode factor analysis of August 1975
Hamilton Harbour sediment samples

VARIABLE	COMMUNALITY	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5
Cu	0.96405	0.2497	-0.9206	0.0567	0.1904	0.1213
Cr	0.93342	0.1931	-0.9369	-0.0875	0.0347	0.0975
Fe	0.98363	0.2789	-0.9478	0.0425	-0.0340	-0.0669
Mn	0.91389	0.6749	-0.6487	0.1754	0.0219	0.0793
Zn	0.95478	0.9433	-0.2291	-0.0062	-0.0536	0.0981
Ni	0.92289	0.1300	-0.9406	0.1042	0.0775	-0.0665
Pb	0.93862	0.9110	-0.3137	-0.0300	-0.0266	0.0935
Cd	0.89111	0.9133	-0.0887	0.0812	0.2033	0.0359
Hg	0.83520	0.7889	-0.3620	0.0883	0.2562	0.0911
COD	0.68224	0.4739	-0.6398	-0.0605	0.1512	-0.1476
TKN	0.90497	0.2730	-0.1617	-0.1622	0.8819	-0.0160
Total P	0.80640	0.7358	-0.2183	0.1789	0.4304	-0.0072
LOI	0.91143	0.5998	-0.4255	0.0562	0.6029	-0.0633
Co	0.85534	0.1561	-0.7484	0.4098	0.3207	-0.0114
Extract- able P	0.76653	0.7912	-0.1126	0.1829	0.3067	0.0181
Al	0.89265	0.0867	0.0490	0.6646	0.6191	0.2403
Ca	0.90853	-0.1549	0.1502	-0.9116	0.1695	0.0473
Mg	0.97154	0.1781	0.2375	0.0294	0.0275	0.9390

TABLE 10

RATIOS OF METAL CONCENTRATIONS BETWEEN
NEARBY SHALLOW AND DEEP ZONES
HAMILTON HARBOUR, JUNE 1975.

<u>Location</u>	<u>Mn</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>Cd</u>	<u>Hg</u>	<u>Pb</u>
252	.31	.22	.47	.26	.10	.05	<.09	.16	.04
254									
253	.24	.25	.37	.36	.13	.26	.21	.21	.21
254									
264	.34	.33	.42	.34	.35	.09	.31	.13	.14
270									

TABLE 11

SHALLOW ZONES EXHIBITING HIGHEST POLLUTANT
CONCENTRATIONS, HAMILTON HARBOUR, 1975

PARAMETER	June		August		Surface: Bottom Ratio
	Station	Concentration (Surface)	Station	Concentration (Surface)	
Cr	2	1195	2	1125	-
	268	250	256	313	2.6
	256	234			
Mn	2	3270	2	3200	-
	262	2200	262	2400	3.7
	256	1540			
Fe (mg/g)	2	445	2	441	-
	262	139	262	115	6.4
	256	84	256	84	3.2
Co	2	21	2	22	-
Ni	2	183	2	190	-
	268	57	268	42	2.1
			256	40	2.0
Cu	2	364	2	350	-
	268	169	256	98	1.7
	256	106			
Zn	262	7800	262	5900	35.3
	2	3900			
Cd	262	12	262	7.8	>13.6
	270	12	256	8.4	3.4
Hg	2	1.2	262	1.0	18.2
	262	1.0	2	0.75	-
Pb	262	1100	262	670	26.1
	2	680			

Note: All results in ug/g unless otherwise stated.

TABLE 12

Factor analysis of replicate samples,
June, 1975. Stations 252, 20, 258, 259

VARIABLE	COMMUNALITY	FACTOR 1	FACTOR 2	FACTOR 3
252A	0.83819	0.3462	-0.7963	0.2904
252C	0.84146	0.3388	-0.8002	0.2938
252D	0.79219	0.2736	-0.8042	0.2656
20A	0.77951	0.3616	-0.4776	0.6485
20C	0.79917	0.4967	-0.3447	0.6585
20E	0.85758	0.2704	-0.2906	0.8367
259A	0.77978	0.7607	-0.3278	0.3060
259B	0.79840	0.7850	-0.2449	0.3496
259C	0.71987	0.5477	-0.5750	0.2988
258A	0.87200	0.8347	-0.3352	0.2510
258B	0.83377	0.8230	-0.3223	0.2294
258C	0.87675	0.8441	-0.3146	0.2556

TABLE 13

Factor analysis of replicate samples,
August 1975. Stations 252, 20, 258, 259

VARIABLE	COMMUNALITY	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
252A	0.85357	0.2502	0.8276	0.1164	-0.3042
252B	0.86306	0.1608	0.8549	0.2833	-0.1616
252C	0.85476	0.3150	0.4139	0.7276	-0.2342
258A	0.86648	0.3917	0.2887	0.1453	-0.7801
258B	0.85130	0.4278	0.2939	0.2229	-0.7296
258C	0.86646	0.5245	0.2430	0.2214	-0.6952
259A	0.84242	0.3128	0.2797	0.5070	-0.6397
259C	0.88359	0.3814	0.1969	0.5520	-0.6282
259E	0.83504	0.4158	0.1846	0.5022	-0.6131
20A	0.86607	0.7678	0.2492	0.2341	-0.3997
20C	0.90438	0.7676	0.2336	0.2868	-0.4223
20E	0.91509	0.7844	0.2327	0.2845	-0.4059

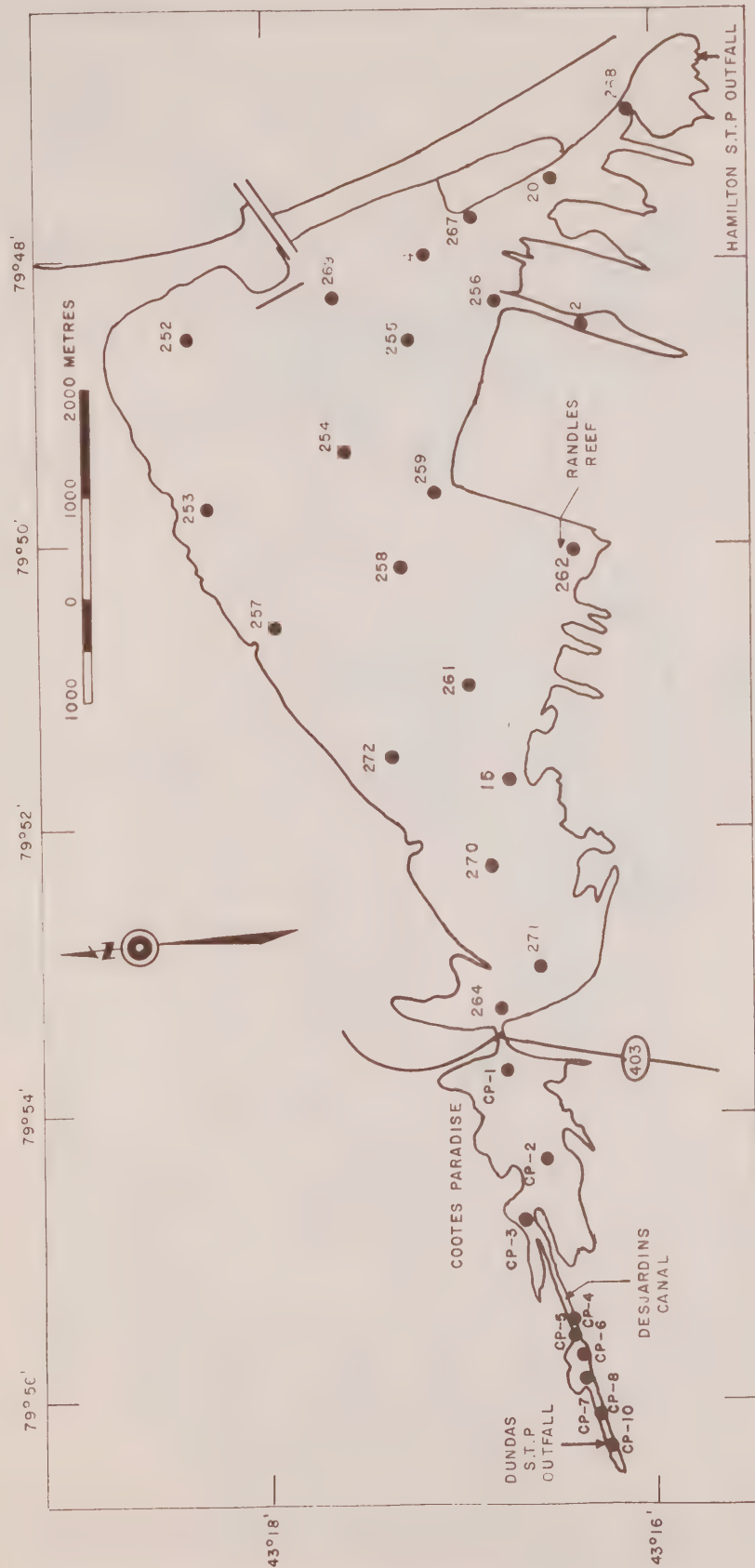


FIGURE 1: JUNE 1975 HAMILTON HARBOUR AND COOTES PARADISE, SEDIMENT SAMPLING LOCATIONS



FIGURE 2: DISTRIBUTION OF TOTAL PHOSPHORUS (mg/g dry wt) HAMILTON HARBOUR
SEDIMENTS—MAY 1975

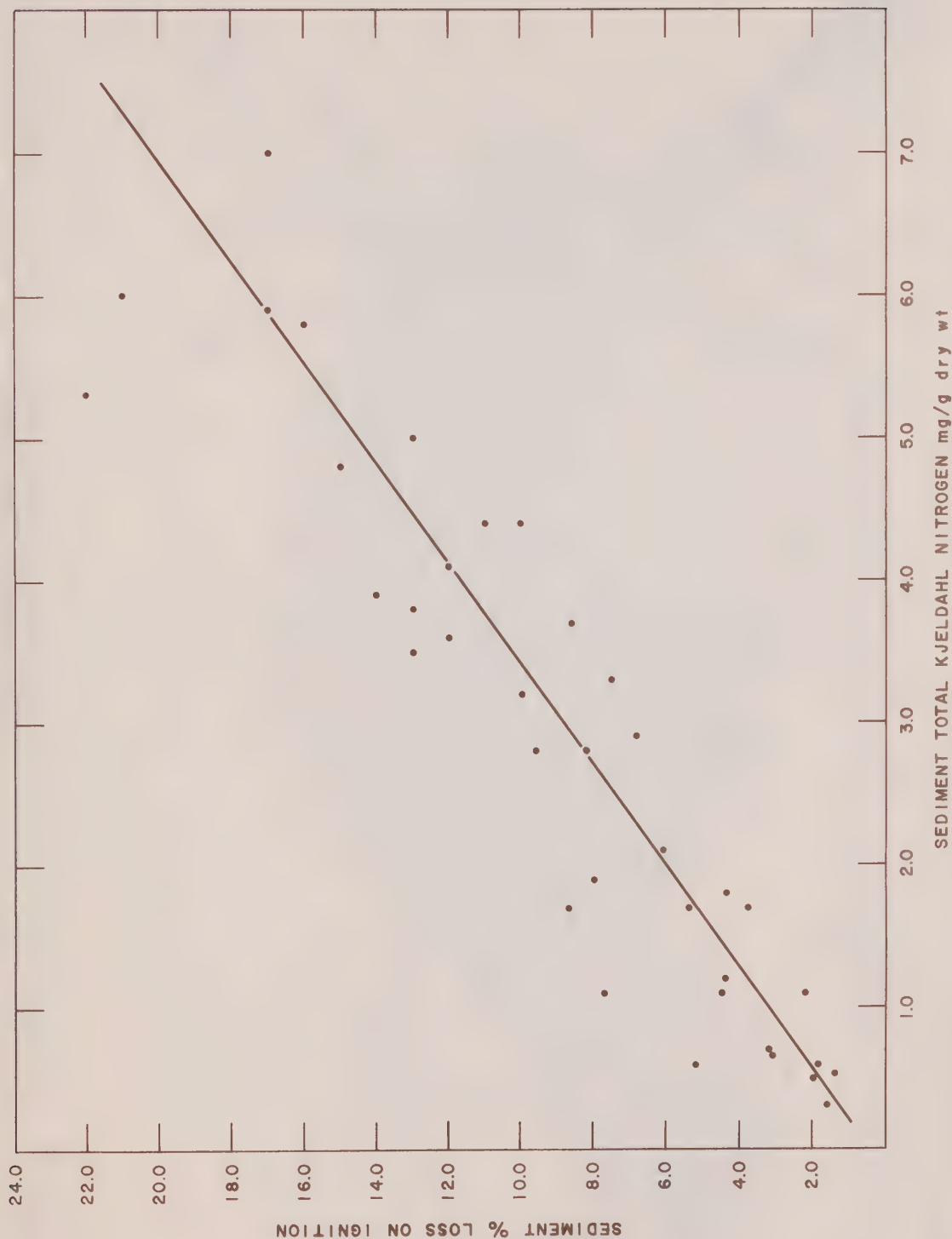


FIGURE 3 - RELATIONSHIP BETWEEN LOSS ON IGNITION AND TOTAL KJELDAHL NITROGEN IN HAMILTON HARBOUR SEDIMENTS (MAY, JUNE 1975 SAMPLES)

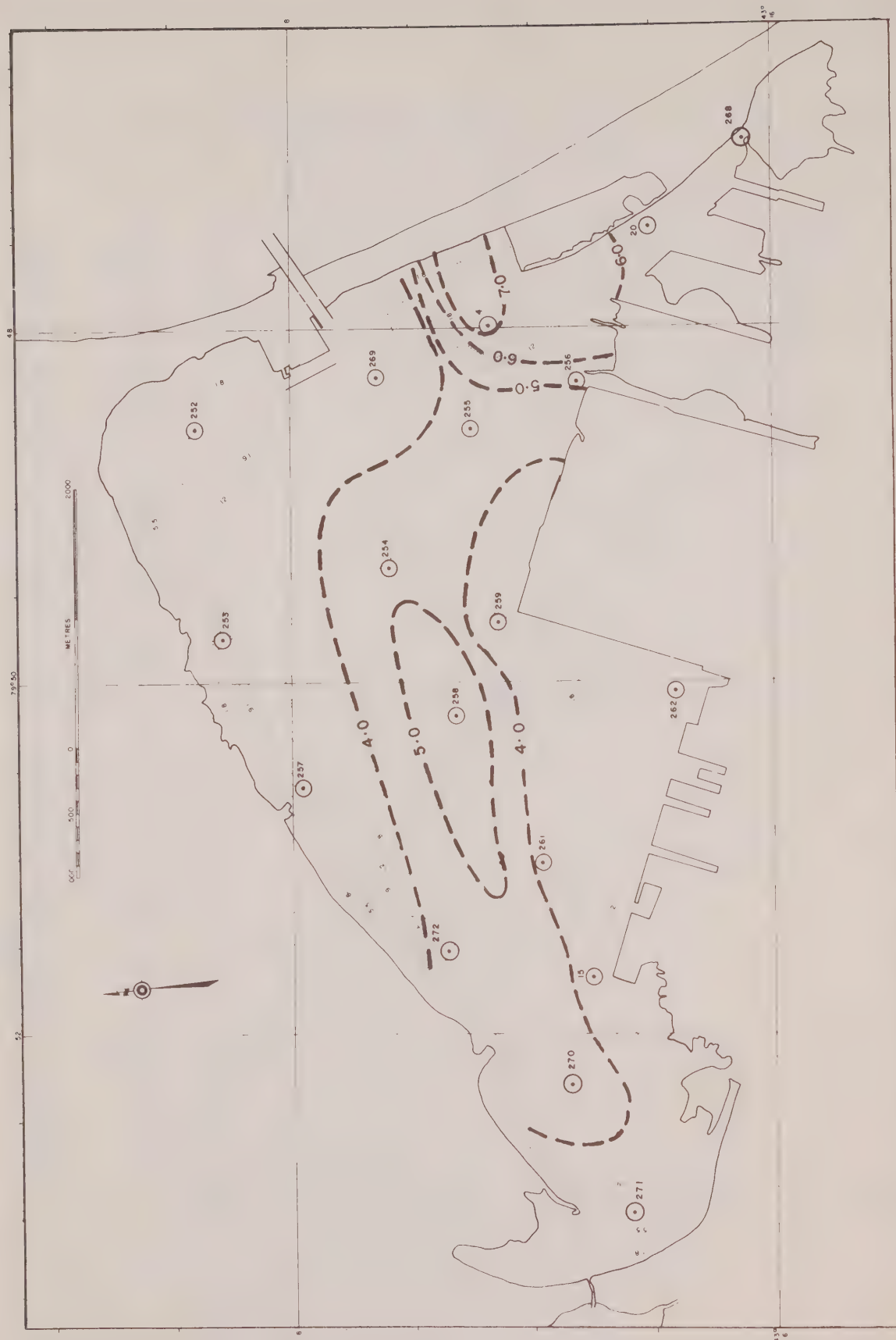
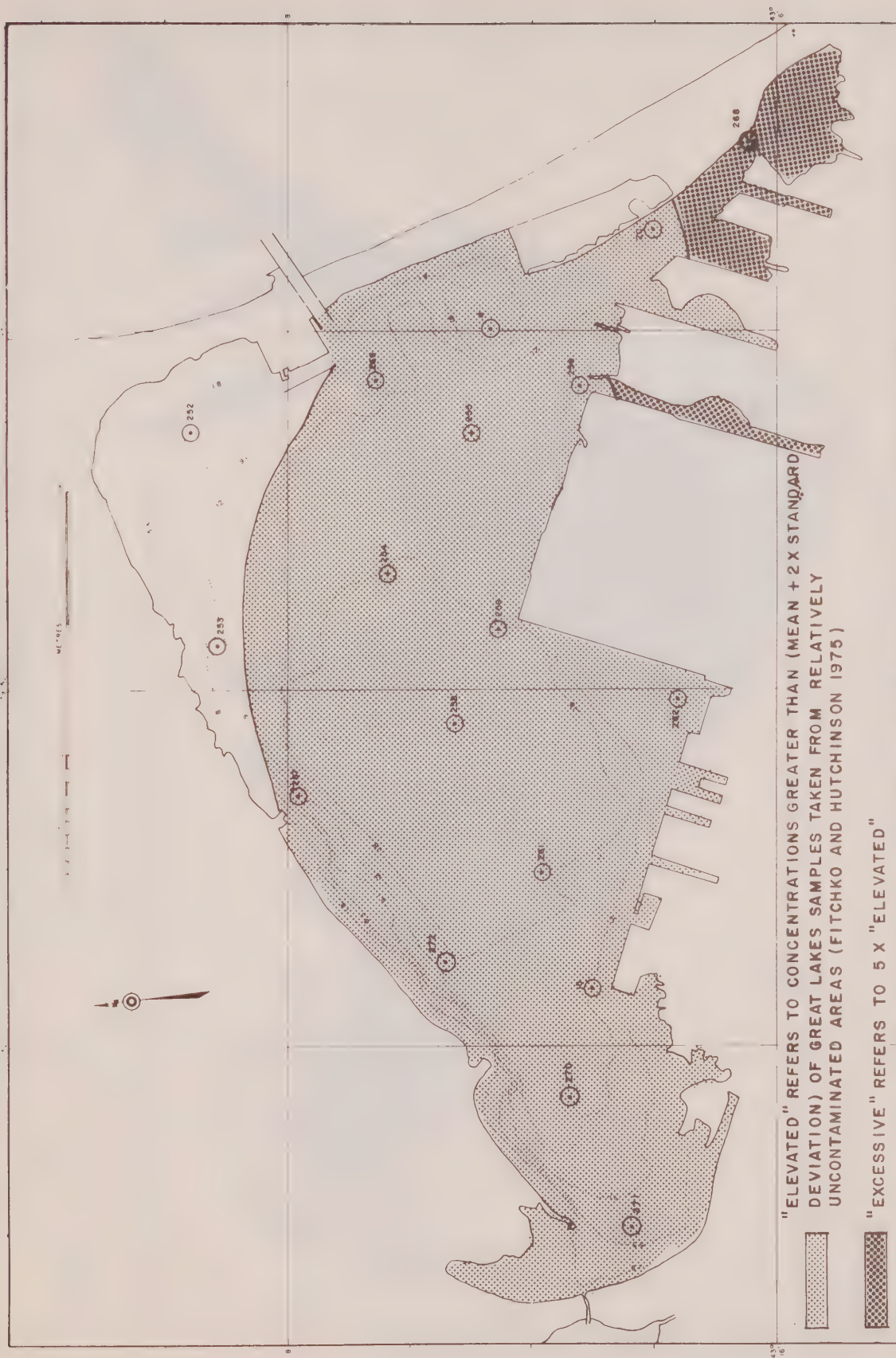
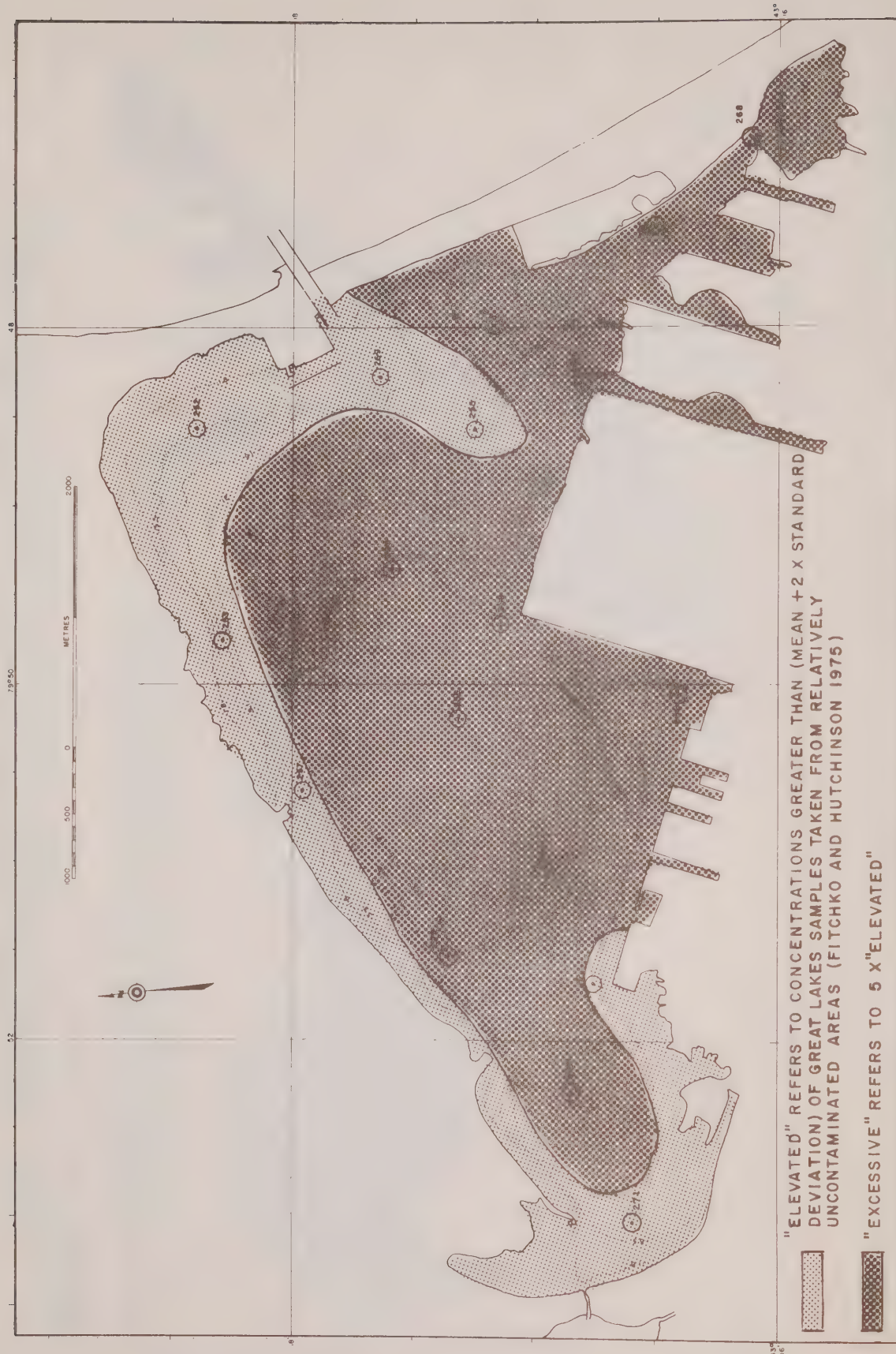


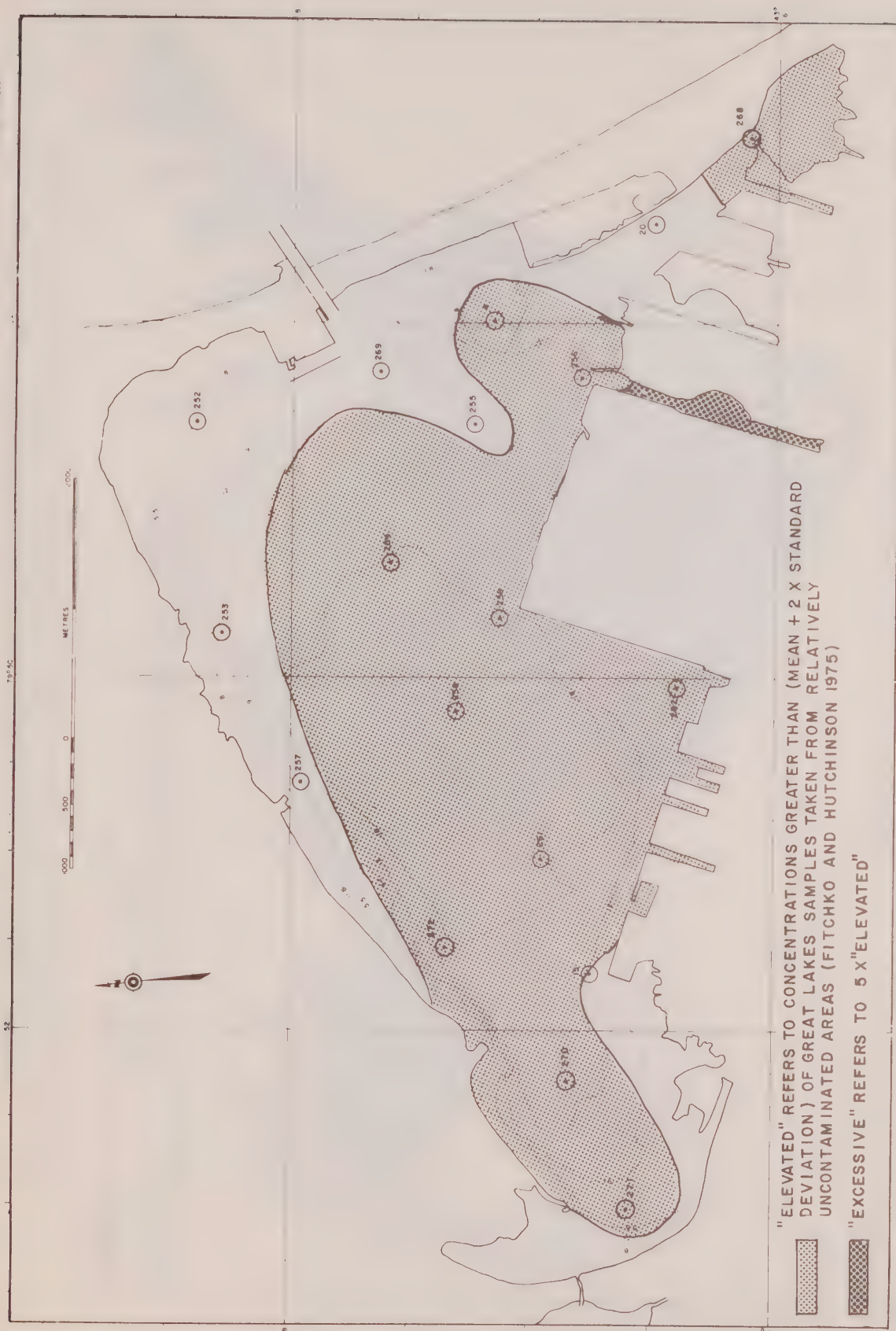
FIGURE 4: DISTRIBUTION OF TOTAL KJELDAHL NITROGEN (mg/g dry wt) IN HAMILTON HARBOUR SEDIMENTS—MAY 1975



**FIGURE 5 : ZONES OF "ELEVATED" AND "EXCESSIVE" CONCENTRATION OF COPPER
JUNE - AUGUST 1975 HAMILTON HARBOUR SURFACE SEDIMENTS**



**FIGURE 6: ZONES OF "ELEVATED" AND "EXCESSIVE" CONCENTRATION OF CHROMIUM
JUNE - AUGUST 1975 HAMILTON HARBOUR SURFACE SEDIMENTS**



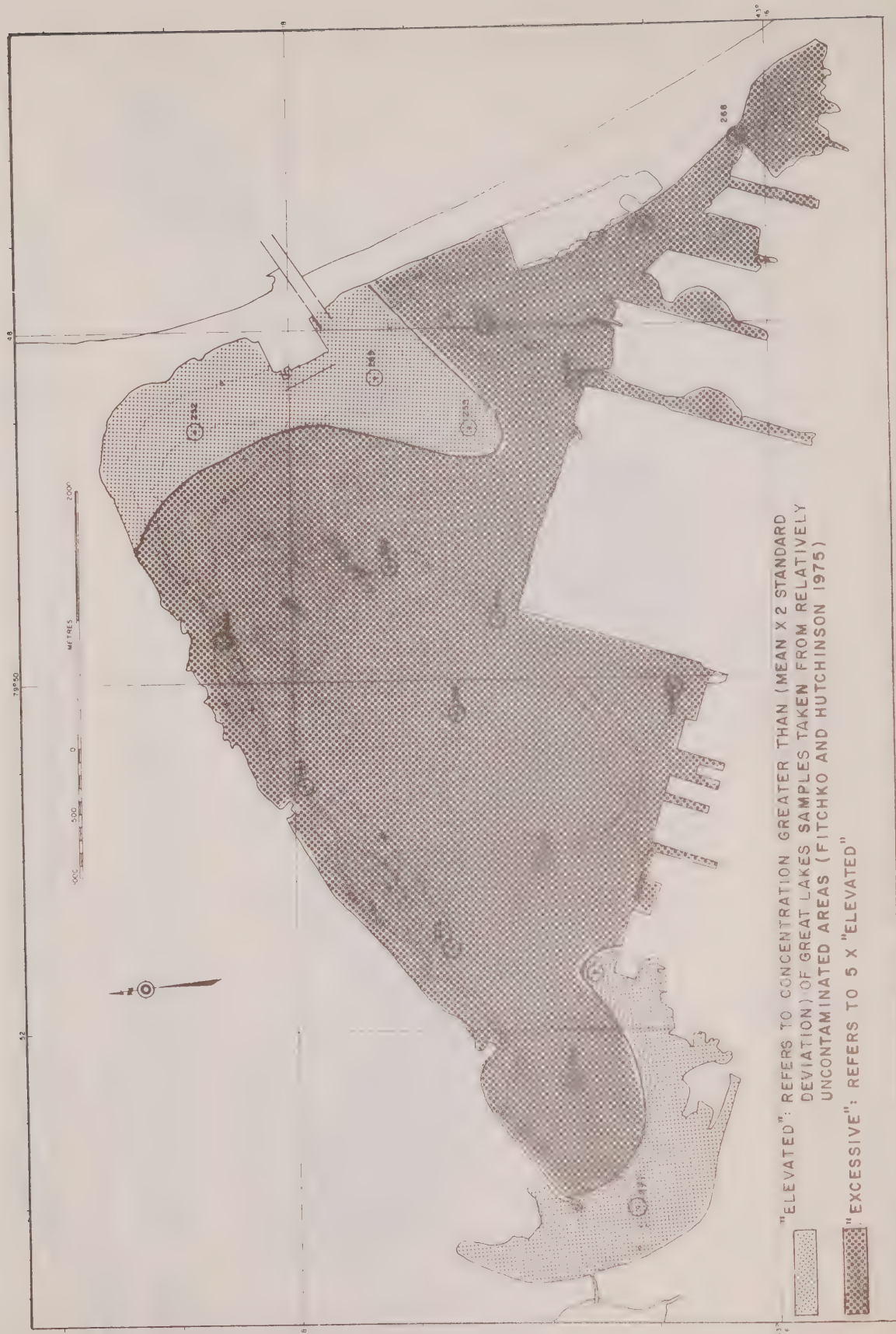
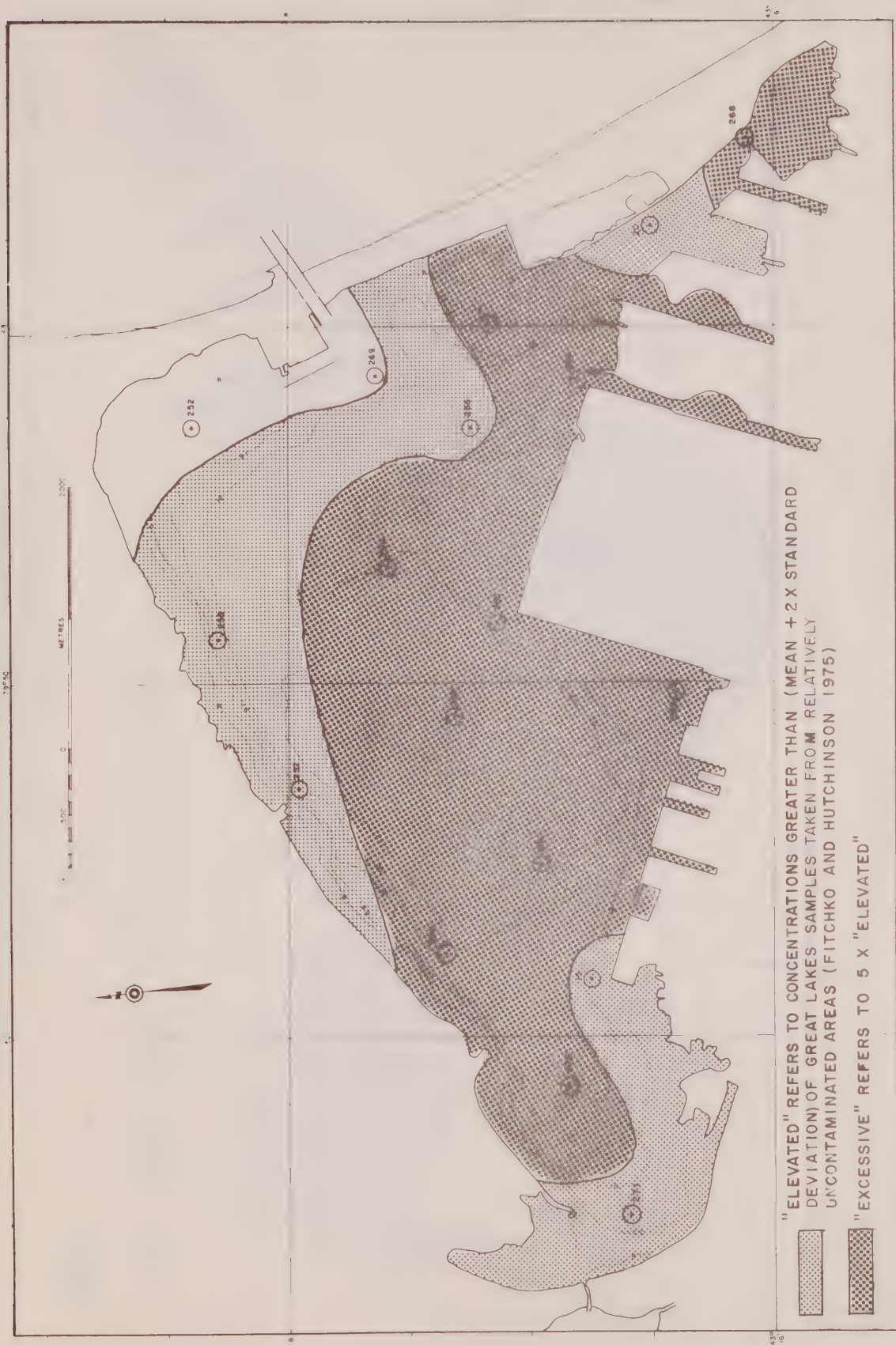


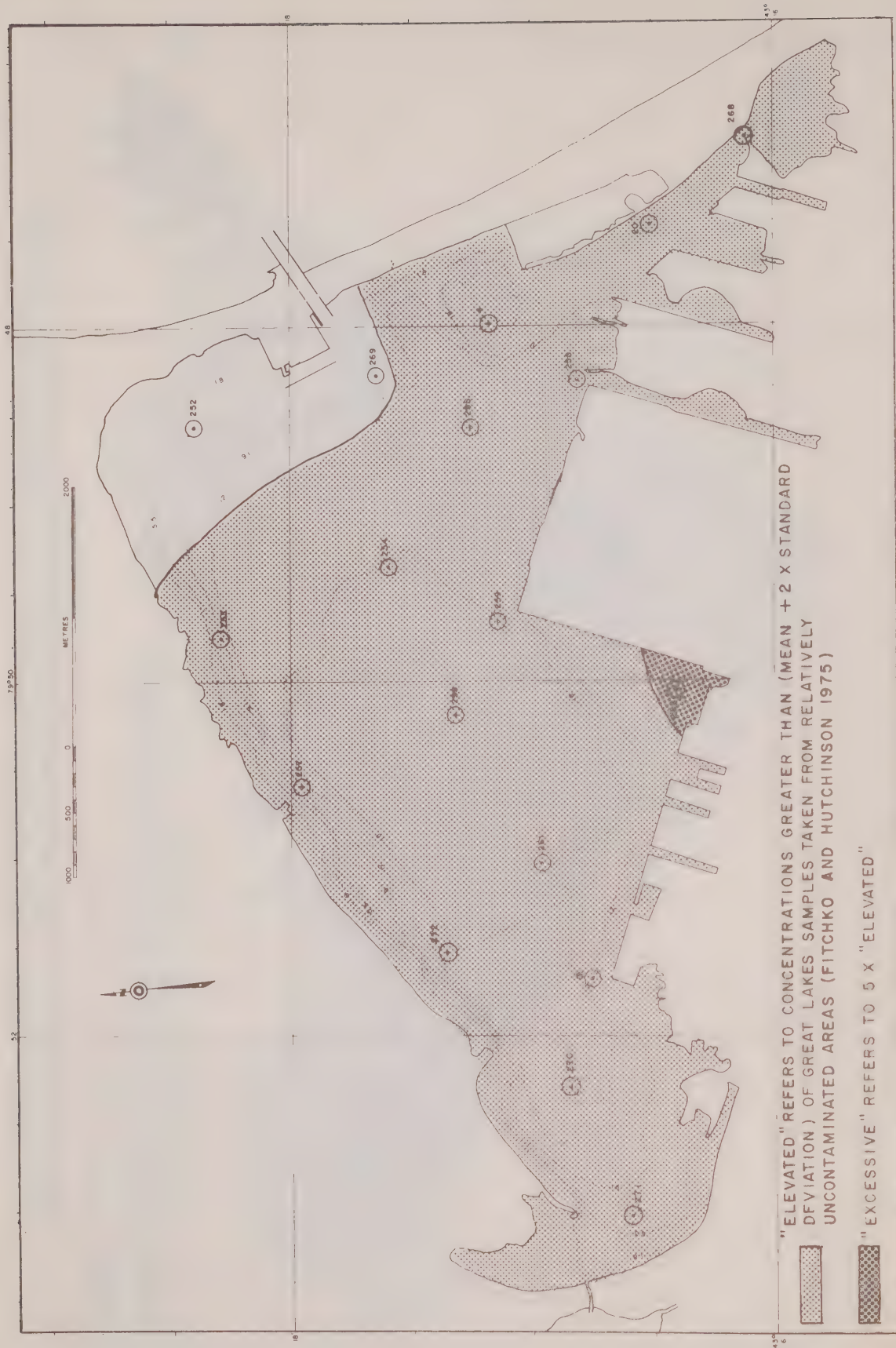
FIGURE 8 : ZONES OF "ELEVATED" AND "EXCESSIVE" CONCENTRATION OF ZINC
JUNE - AUGUST 1975 HAMILTON HARBOUR SURFACE SEDIMENTS



"ELEVATED" REFERS TO CONCENTRATIONS GREATER THAN (MEAN + 2 X STANDARD DEVIATION) OF GREAT LAKES SAMPLES TAKEN FROM RELATIVELY UNCONTAMINATED AREAS (FITCHKO AND HUTCHINSON 1975)

"EXCESSIVE" REFERS TO 5 X "ELEVATED"

FIGURE 9 : ZONES OF "ELEVATED" AND "EXCESSIVE" CONCENTRATION OF LEAD
JUNE - AUGUST 1975 HAMILTON HARBOUR SURFACE SEDIMENTS



"ELEVATED" REFERS TO CONCENTRATIONS GREATER THAN (MEAN + 2 X STANDARD DEVIATION) OF GREAT LAKES SAMPLES TAKEN FROM RELATIVELY UNCONTAMINATED AREAS (FITCHKO AND HUTCHINSON 1975)

"EXCESSIVE" REFERS TO 5 X "ELEVATED"

FIGURE 10: ZONES OF "ELEVATED" AND "EXCESSIVE" CONCENTRATIONS OF CADMIUM
JUNE - AUGUST 1975 HAMILTON HARBOUR SURFACE SEDIMENTS

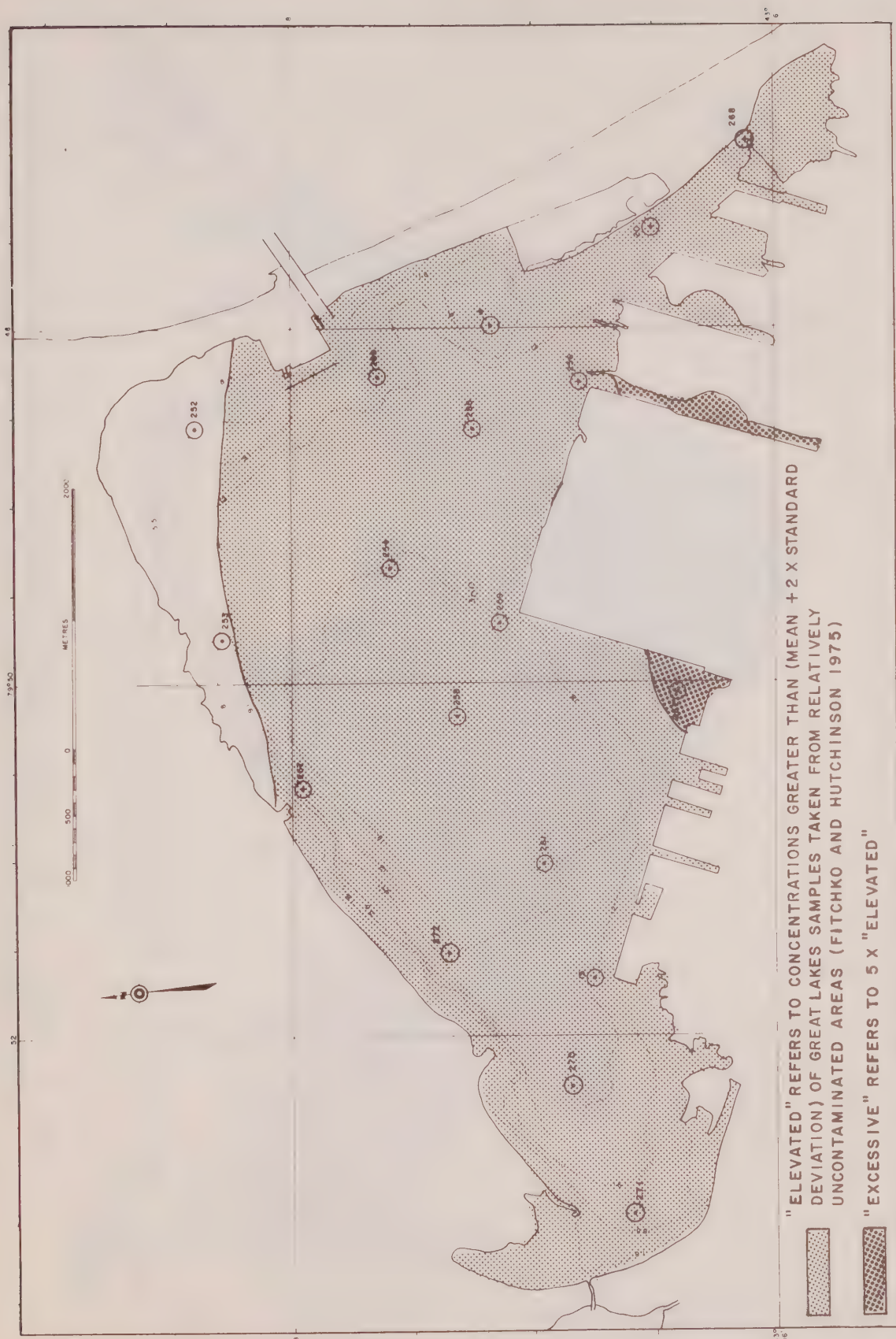


FIGURE 11: ZONES OF "ELEVATED" AND "EXCESSIVE" CONCENTRATION OF MANGANESE
JUNE - AUGUST 1975 HAMILTON HARBOUR SURFACE SEDIMENTS

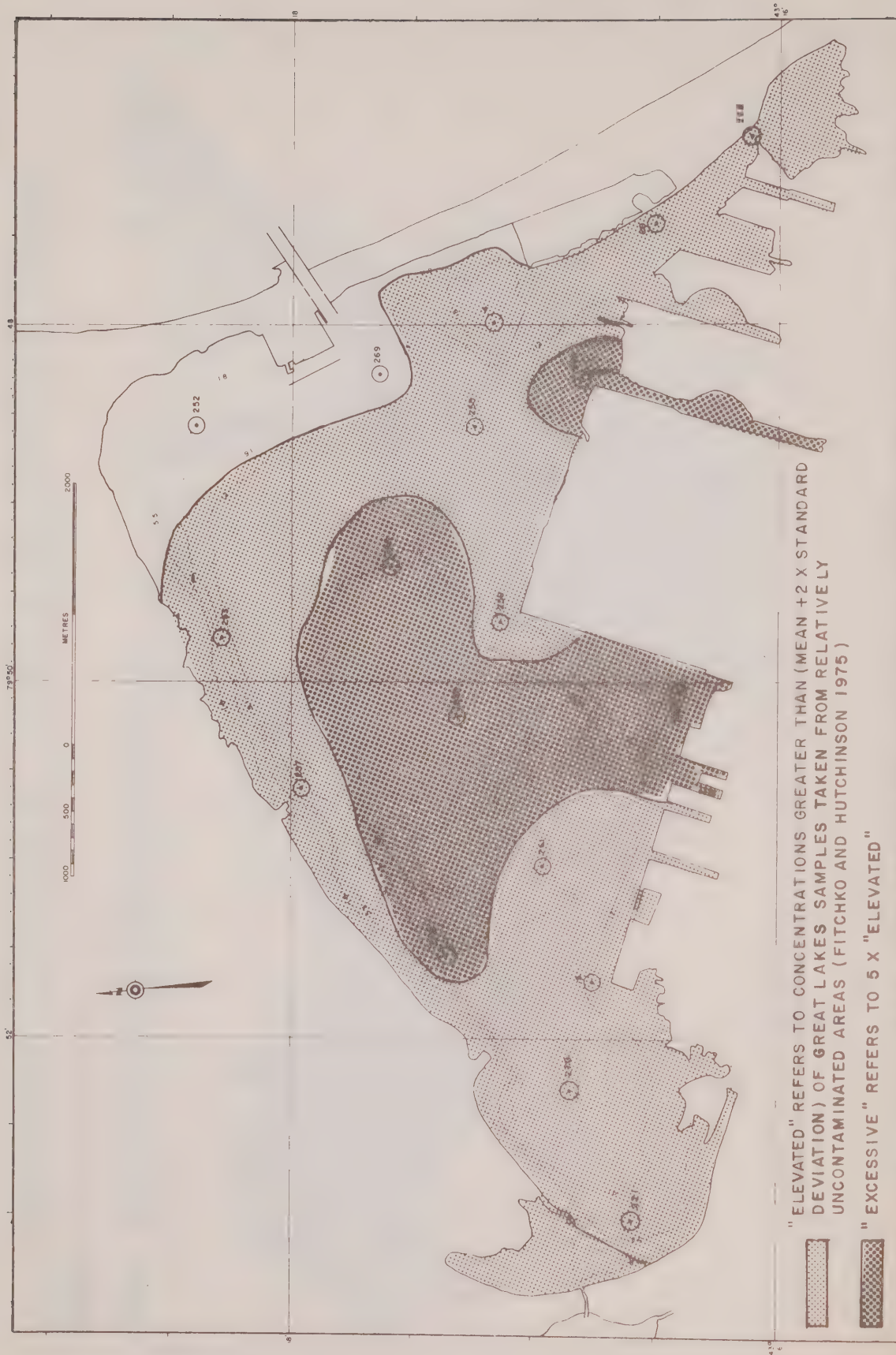


FIGURE 12: ZONES OF "ELEVATED" AND "EXCESSIVE" CONCENTRATION OF MERCURY
JUNE - AUGUST 1975 HAMILTON HARBOUR SURFACE SEDIMENTS



FIGURE 13: MAY 1975 HAMILTON HARBOUR SEDIMENTS, 6 FACTORS

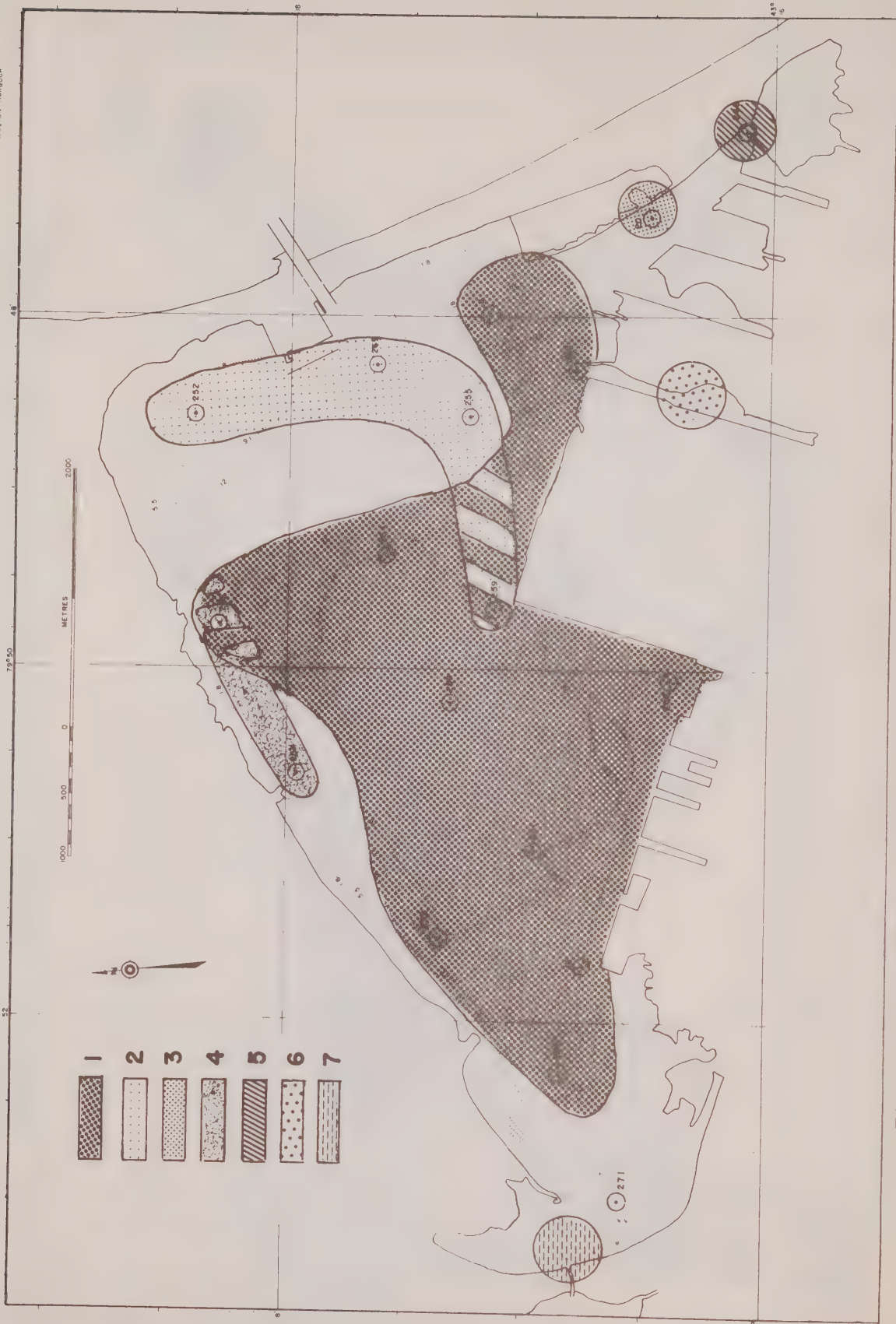


FIGURE 14 : JUNE 1975 HAMILTON HARBOUR SEDIMENTS, 7 FACTORS

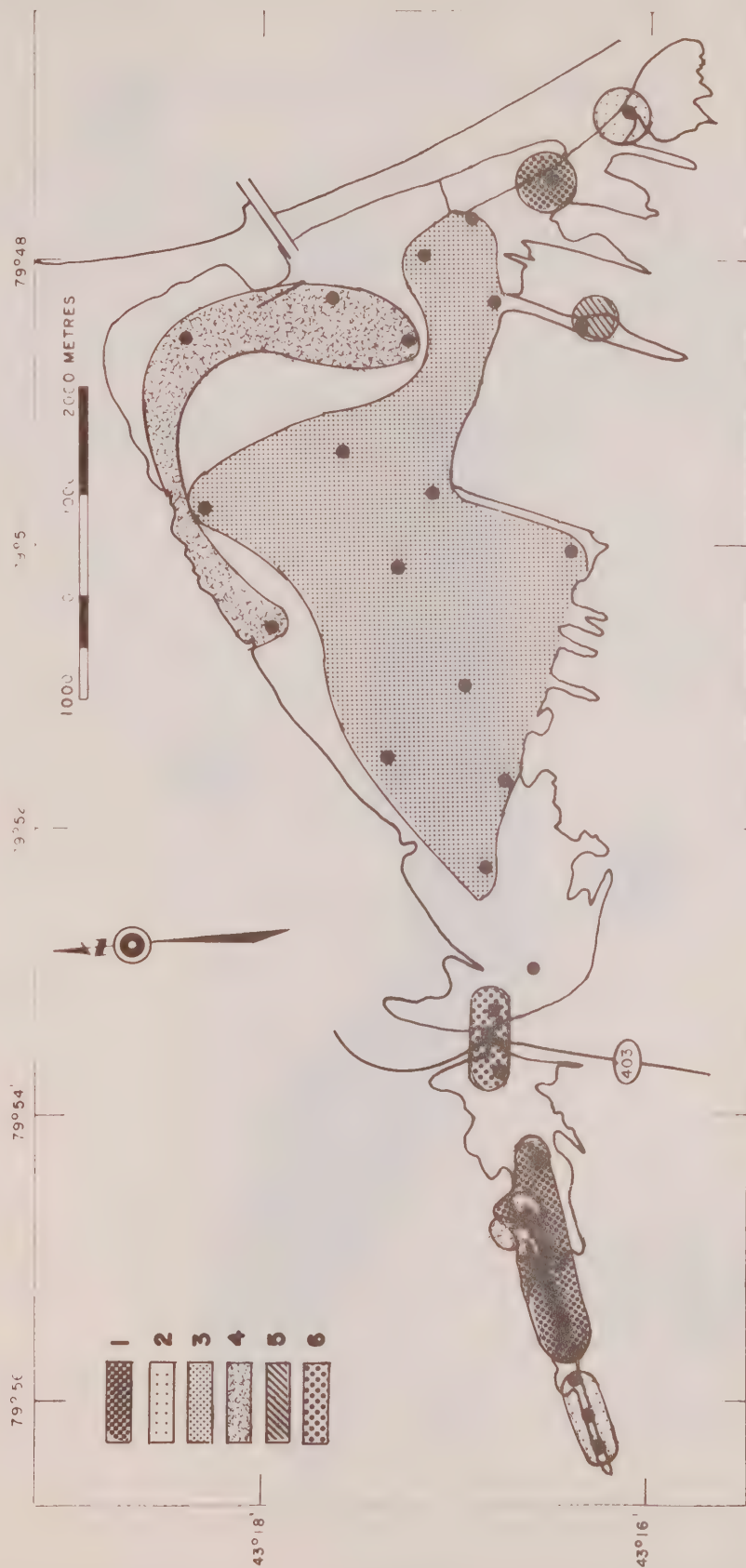


FIGURE 15 : JUNE 1975 HAMILTON HARBOUR AND COOTES PARADISE,
6 FACTORS

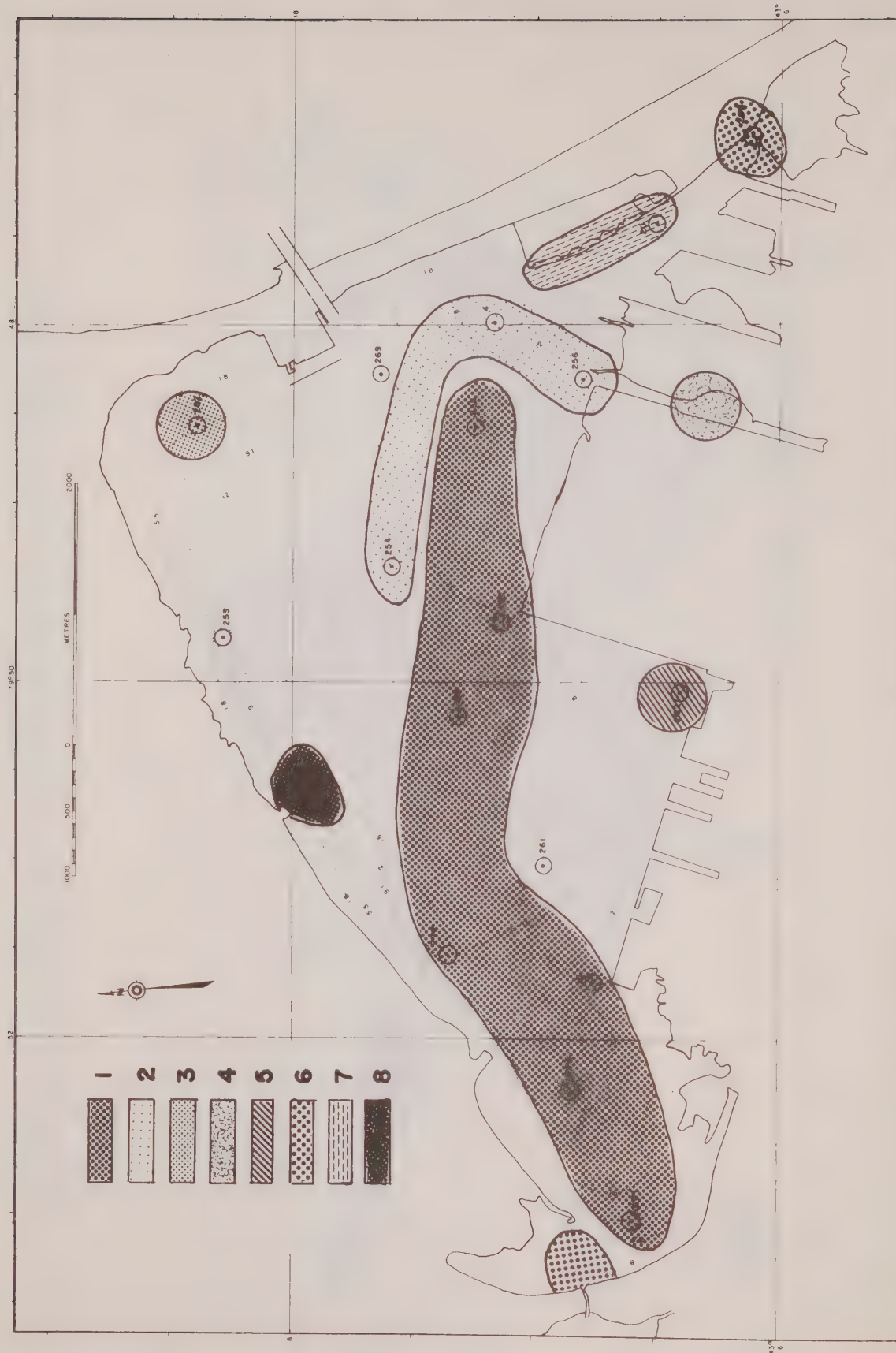


FIGURE 16 : AUGUST 1975 HAMILTON HARBOUR SEDIMENTS, 8 FACTORS

APPENDIX 1

EVALUATION OF SIMILARITY COEFFICIENT

In order to determine the degree of similarity between various members of a series of sediment samples, a statistical technique called "ratio matching" originally developed by Anders of Dow Chemical Co. was modified. This technique is based on the fact that sediment samples of common origin will tend to have similar ratios of concentrations of trace pollutants (heavy metals, PCB, etc.) whereas the absolute concentrations of these individual pollutants may vary considerably due to dilution with inert materials such as SiO_2 and CaCO_3 . This technique could also be used for developing generic relationships between individuals such as biological communities based on species populations.

For each sample, Anders divides the concentration of each chemical parameter by that of each other parameter to obtain the "concentration ratio matrix", $\{X_{ij}\}$, which is a triangular matrix of size $m \times m$, where m is the number of chemical parameters involved. Two samples A and B are compared by means of the ratio matrix $\{Y_{ij}(AB)\}$, which is generated by dividing each element of the $\{X_{ij}\}_A$ matrix by the corresponding element of the $\{X_{ij}\}_B$ matrix. The ratio matrix of A and B is thus:

$$\{Y_{ij}(AB)\} = \begin{bmatrix} \frac{X_{11}(A)}{X_{11}(B)} & & & \\ \frac{X_{21}(A)}{X_{21}(B)} & \frac{X_{22}(A)}{X_{22}(B)} & & \\ \frac{X_{31}(A)}{X_{31}(B)} & \frac{X_{32}(A)}{X_{32}(B)} & \text{-----} & \\ \vdots & \vdots & & \\ \frac{X_{m1}(A)}{X_{m1}(B)} & \frac{X_{m2}(A)}{X_{m2}(B)} & \text{-----} & \frac{X_{mm}(A)}{X_{mm}(B)} \end{bmatrix}$$

Here, each X_{ij} represents an element of an $\{X_{ij}\}$ matrix, and there are $\frac{n}{2}$ Y matrices, where n is the number of samples involved.

If two sediment samples have similar origin, then the ratios of the pollutant concentrations of interest will have similar values, and thus the Y_{ij} values will be close to 1. Consequently, we have defined the similarity coefficient as an evaluation of the relative differences of all $\{Y_{ij}\}$ (kl) matrix elements from 1. For each of the $\binom{m}{2}$ off-diagonal elements in the $\{Y_{ij}\}$ (kl) matrix, the absolute value of the logarithm is used as a measure of the difference of the element from 1. As the similarity is inversely related to the difference of each element from 1, and a value of 1.0 is desired for a perfect correlation (all $\{Y_{ij}\}$ values = 1.0), 1.0 is added to the logarithms, and the similarity coefficient takes the form

$$Z_{k\ell} = \frac{\sum_{i=1}^m \sum_{j=i+1}^m \left[\frac{1}{|\ln \{Y_{ij}\} (kl)| + 1} \right]}{\binom{m}{2}}$$

In this equation, k and ℓ vary from 2 to n, where n is the number of samples, $Z_{kk} = 1$ and $Z_{k\ell} = Z_{\ell k}$.

These similarity coefficients $Z_{k\ell}$ form a "correlation matrix" of size n x n, as follows:

$$\{Z_{k\ell}\} = \begin{bmatrix} 1 & & & & \\ Z_{AB} & 1 & & & \\ Z_{AC} & Z_{BC} & 1 & & \\ \vdots & \vdots & & \ddots & \\ Z_{An} & Z_{Bn} & \cdots & \cdots & 1 \end{bmatrix}$$

This matrix of similarity coefficients is analyzed for statistical significance by the method presented in the main part of this section, and for large matrices containing many significant coefficients, factor analysis is used to discern groupings of related samples.

Appendix II

Table A-1

ANALYSES OF MAY 1975 HAMILTON HARBOUR SEDIMENT SAMPLES

Station No.	BOD	COD*	LOI(%)	TKN*	P	Cr	Mn*	Fe*	Co	Ni	Cu	Zn*	Cd	Hg	Mo	Pb
252	.76	25	2.2	1.1	1.7	37	.468	15.1	6.7	16	22	.516	2.3	.46	1.9	33
20	12	230	16	5.8	6.2	480	1.54	116	19	33	213	5.03	12	7.3	8.7	478
256	10	260	21	6	3	380	2.34	124	17	58	144	3.42	6.6	3.4	8.4	393
4	5.9	270	17	7	6	440	3.59	115	16	68	169	4.23	12	4.8	7.6	514
269	.33	40	3.1	.66	.84	24	.599	15.5	8	13	19	.165		.16	1.2	21
255	6.2	170	12	4.1	4.1	310	2.33	81.4	17	52	138	3.27	7.8	.27	3.9	346
254	5.8	210	15	4.8	4.8	360	2.43	119	19	61	161	5.26	12	5.6	4.8	535
258	10	255	17	5.9	5.3	400	3.07	136	22	68	172	6.51	16	6.2	4.6	667
264	.14	45	3.2	.7	.84	27	.66	21.1	9.9	23	37	6.72	2.8	.068	1.3	70
260	1.7	140	10	4.4	5.3	180	1.99	75.1	18	58	104	3.33	9.3	.52	2.9	335
270	2.6	160	11	4.4	3.8	170	1.53	65.1	18	56	121	3.36	13	3.8	2.9	370
15	1.1	75	5.4	1.7	2.1	88	1.03	35.6	13	26	59	1.58	5.6	1.4	1.8	182
261	5.4	195	13	3.8	4.2	253	2.03	89.1	19	56	144	4.58	16	3.9	3.1	510
262	5.2	150	8	1.9	1.3	67	1.27	55.8	12	28	57	1.95	4.6	3.6	2.0	486
263	2.6	205	13	5	4.3	290	2.27	92.6	21	65	158	5.21	15	4.6	3.3	553
257	1.8	70	4.41	1.8	3.1	89	1.09	37.3	11	29	45	1.18	3.7	1.2	2.5	135
253	1.3	90	6.8	2.9	3.8	191	1.26	56.8	15	46	87	2.7	7.6	.69	2.0	267
1030	0.12	20	2.0	0.5	0.6	15.6	.559	14.2	8.5	12	17	.087	0.15	0.021	0.9	23
268	3.6	285	22.	5.3	3.0	132	.608	24.4	14	65	67	.681	2.4	0.24	2.3	136
259	2.2	145	7.5	3.3	2.7	184	2.75	79.6	16	38	87	3.33	7.2	0.63	2.9	369

Note: * These results are in mg/g. All other results are in $\mu\text{g/g}$, unless otherwise stated.

TABLE A2
ANALYSES OF JUNE 1975
HAMILTON HARBOUR SEDIMENT SAMPLES

Station No.	Top or Bottom Portion	Cr	Cu	Ni	Zn	Pb	Cd	Mn	Fe*	Hg	Co	COD*	LOI (%)	TKN*	Total P*	Al*	Ca*	Mg*
252A	T	18	10	14	117	16	0.5	431	18.6	0.04	3.0	25	1.9	0.59	1.0	8.72	49.6	7.34
252A	B	13	15	11	40	7.3	0.5	620	18.5	0.01	7.0	35	2.4	0.91	0.74	9.77	63.6	8.46
252B	T	22	15	13	174	17	0.5	532	18.7	0.05	6.0	20	1.8	0.75	1.0	9.19	50.5	7.22
252C	T	13	12	11	71	7.5	0.5	539	17.0	0.03	6.5	30	2.4	0.78	0.91	8.53	59.1	8.09
269A	T	17	16	8.5	162	22	0.5	595	13.5	0.06	5.5	10	1.4	0.53	0.64	4.91	53.0	4.96
269A	B	35	42	19	337	47	0.5	770	25.7	0.20	9.0	60	4.6	1.2	0.98	8.96	51.0	7.34
269B	T	26	26	15	229	30	0.5	620	19.5	0.06	6.0	50	3.4	0.73	0.82	6.39	47.0	5.72
269B	B	19	29	16	149	24	0.5	632	22.2	0.11	7.0	70	6.2	1.3	0.63	9.07	46.7	5.95
269C	T	18	23	14	164	29	0.5	592	17.9	0.03	5.0	20	1.8	0.74	0.73	7.11	45.8	5.96
269C	B	21	31	17	192	34	0.5	615	23.9	0.12	7.5	60	4.2	1.4	0.78	10.6	45.7	6.84
267A	T	173	78	25	1490	180	2.8	1160	53.3	0.41	6.0	85	5.4	2.5	2.5	8.88	56.7	6.34
267B	T	184	99	29	1510	184	3.0	1310	58.1	0.44	7.0	110	6.4	2.7	2.4	9.65	63.6	7.46
20A	T	33	24	8.3	192	32	0.5	762	14.9	0.06	3.0	60	3.8	1.7	0.81	3.70	23.5	6.34
20A	B	30	7.0	6.0	22	2.0	0.5	767	5.3	0.005	4.5	80	5.5	1.7	0.22	2.31	30.6	6.72
20B	T	94	48	19	654	94	1.0	1000	33.0	0.18	3.0	90	5.3	2.7	1.6	5.34	19.7	6.59
20B	B	8.0	11	4.0	23	6.5	0.5	797	5.69	0.005	4.5	95	6.9	2.9	0.24	2.52	299	6.95
20C	T	56	34	13	349	5.4	0.5	857	2.26	0.010	3.0	60	3.5	2.1	1.2	3.68	196	6.46
20C	B	8.0	8.5	4.5	19	1.0	0.5	705	5.1	0.005	3.0	90	5.4	2.2	0.20	2.03	302	6.46
268A	T	240	159	56	1260	255	7.0	785	4.24	0.41	13	120	8.6	3.7	3.2	10.1	58.6	11.9
268B	T	260	178	57	1270	271	7.8	790	4.47	0.38	12	130	9.7	3.6	3.5	19.4	57.5	13.4
256A	T	206	92	35	2500	363	6.0	1240	75.9	0.76	7.5	130	10	3.2	2.0	9.84	90.4	7.72
256B	T	350	150	4.0	3420	369	6.3	2100	118	0.96	11	170	12	3.9	3.7	11.8	66.0	8.47
256C	T	146	77	28	1480	173	4.0	1270	59.0	0.40	6.0	85	7.1	1.9	1.6	8.63	78.3	8.84
2A	T	1200	246	169	4390	782	4.5	3230	420	1.6	21	380	15	2.4	2.5	3.61	22.3	4.02
2B	T	1100	381	197	3360	581	3.0	3300	469	0.75	21	380	15	2.6	2.6	3.66	24.6	4.14
4	T	173	78	35	2020	246	4.3	1480	651	0.43	8.3	75	6.1	2.1	2.1	9.38	50.4	7.90
255	T	8.0	7.0	7.3	98	15	0.5	613	14.8	0.02	4.5	10	1.6	0.31	0.60	3.93	58.8	4.89
255	B	99	84	30	615	114	4.7	763	45.1	0.08	7.0	100	7.7	2.5	1.4	8.41	122	7.44
259A	T	72	35	20	1010	148	3.0	1340	37.5	0.17	6.0	70	4.5	1.1	1.0	7.15	52.3	7.00
259B	T	221	97	46	3730	410	8.0	2460	94.5	0.70	11	210	13	3.1	3.2	10.8	46.6	8.13
259C	T	36	34	25	465	63	1.0	1010	27.3	0.17	9.3	55	5.4	0.69	0.99	11.6	83.0	12.2

TABLE A2, Continued

Station No.	Top or Bottom Portion	Cu	Ni	Zn	Pb	Cd	Mn	Fe*	Hg	Co	COD*	LOI(%)	TKN*	Total P*	Al*	Ca*	Mg*
262A	T	107	40	7210	1300	12	1690	120	1.3	8.5	280	14	3.9	2.1	10.8	47.4	9.5
262B	T	141	40	8500	1060	12	2560	157	0.60	11	290	18	4.0	2.8	9.81	47.5	8.10
262C	T	135	36	7700	963	11	2350	139	1.1	9.5	295	15	3.8	2.6	9.68	46.3	9.90
261	T	129	84	40	359	8.3	1400	55.5	0.51	9.3	110	8.2	2.8	2.5	11.5	41.9	8.08
15A	T	39	42	771	104	4.8	811	32.5	0.24	6.5	50	4.4	1.2	1.9	8.26	40.9	6.95
15A	B	37	29	640	135	4.0	949	45.2	0.44	9.5	75	6.8	2.5	1.8	13.8	34.9	8.90
15B	T	34	31	458	72	2.5	743	27.5	0.20	7.0	44	4.4	1.2	1.4	8.38	40.5	6.45
15B	B	8.0	10	67	27	0.5	830	25.1	0.03	8.5	45	4.8	1.6	0.82	11.6	57.5	8.02
270	T	152	61	2990	348	12	1530	73.0	0.58	14	128	12	3.6	2.8	18.6	33.6	10.4
270	B	45	91	815	129	5.0	1150	55.2	0.48	12	100	11	3.7	1.8	18.7	34.0	9.57
271A	T	35	31	533	89	3.0	943	42.2	0.37	11	90	7.8	2.1	1.3	15.3	41.6	10.2
271B	T	50	36	539	80	2.6	936	35.6	0.34	11	90	8.5	2.2	1.4	14.8	41.5	9.98
271C	T	42	33	458	85	2.8	830	40.7	0.37	13	80	8.1	2.3	1.5	14.6	41.1	9.98
264	T	25	21	278	51	3.8	525	24.6	0.08	6.0	70	8.7	1.7	1.1	7.30	49.2	7.42
264	B	38	36	693	99	5.0	831	33.1	0.14	9.8	95	9.2	2.7	1.6	9.20	52.4	9.58
272	T	99	84	1760	214	8.0	1210	57.8	0.56	8.5	130	12	3.2	2.1	12.2	64.2	8.74
258A	T	103	36	1470	194	5.0	1490	61.6	0.66	12	110	9.6	2.8	2.2	13.2	48.8	9.44
258B	T	90	44	1560	214	8.3	1640	73.7	0.87	11	110	11	3.2	2.4	16.1	41.2	9.54
258C	T	117	97	41	1820	7.8	1670	69.8	0.56	12	120	14	3.2	2.7	14.2	45.1	9.39
254	T	167	47	2370	317	11	1610	81.1	0.74	12	130	13	3.5	3.1	14.6	39.4	9.20
253	T	32	17	623	51	2.4	396	20.7	0.16	3.0	20	5.2	0.6	1.1	4.43	32.3	5.07
253	B	11	8.5	148	15	1.0	343	13.8	0.10	3.0	20	5.6	0.6	0.8	3.90	39.7	4.68
257A	T	32	18	493	50	1.5	570	22.0	0.06	3.0	20	7.7	1.1	1.3	4.70	52.1	6.50
257B	T	20	15	256	28	1.5	550	18.9	0.08	3.0	20	7.5	0.8	0.8	4.70	55.7	5.97
257C	T	16	12	213	25	1.5	598	17.4	0.08	3.0	20	6.1	0.6	0.86	4.40	48.7	5.12
257C	B	5.3	5.3	31	2.0	1.0	662	10.4	0.005	3.0	20	13	0.6	0.5	4.00	131	6.15

Table A-3

ANALYSES OF AUGUST 1975 HAMILTON HARBOUR SEDIMENT SAMPLES

Station No.	Top or Bottom Portion	Cu	Cr	Fe*	Mn	Zn	Ni	Pb	Cd	Hg	COD*	TKN*	Total P*	LOI(%)	Co	Acid Extractable P*	Al*	Ca*	Mg*	Sulfide	As
252A	T	11	14	13	425	42	9.0	2.5	0.3	.01	25	.81	.79	2.3	3.0	.74	4.9	60	6.4	10.8	1.8
252B	T	10	18	12	290	44	6.5	2.0	0.3	.01	270	0.1	.73	2.3	3.5	.78	4.7	56	5.5	13.4	1.9
252C	T	14	28	12	370	270	10	30	0.8	.03	20	.16	1.0	2.3	4.0	1.1	3.4	58	6.0	83.5	2.0
257A	T	58	150	44	1100	2100	30	190	4.4	.17	165	1.2	2.1	12	7.0	1.7	7.7	40	3.8	331	12
257B	T	47	116	36	1000	1600	44	160	3.8	.45	55	.62	1.9	4.2	2.0	1.5	6.6	44	7.6	139	9.2
257B	B	9.5	10	9.3	390	40	5.0	2.0	0.3	0.01	6.5	.26	.6	4.2	4.5	.54	3.2	45	5.4	21.6	1.2
257B	B	27	24	21	630	220	13	23	0.7	.18	40	1.5	.84	9.5	8.0	8.5	33	33	3.8	9.3	4.2
272	T	58	72	44	1200	800	28	98	3.0	.93	105	2.9	1.7	9.5	5.0	1.3	13.6	31	6.5	52.5	11
270A	T	78	74	44	1100	870	32	120	4.1	.32	100	2.3	1.8	8.7	10	1.3	16.8	31	7.2	139	11
270B	T	91	91	49	1200	1100	33	140	4.8	.54	100	2.2	1.8	9.0	11	1.4	18.0	30	6.0	167	12
264	T	54	44	22	680	510	28	85	5.2	.17	130	1.7	1.4	8.9	7.0	1.2	7.1	45	4.6	117	6.0
271	T	61	48	34	900	490	26	70	2.0	.39	80	1.8	1.4	7.2	10	1.1	16.1	29	4.9	103	6.8
15	T	50	48	29	780	510	20	75	2.4	.35	65	1.2	1.6	5.5	8.0	1.4	9.8	34	4.2	30	5.5
261	T	86	135	42	1300	2000	54	230	6.4	.46	85	1.6	2.4	6.7	7.0	1.5	8.2	42	5.8	708	11
262A	T	68	104	109	2200	5300	24	600	6.8	.91	200	1.8	1.9	10	8.5	1.5	8.8	49	7.4	2125	12
262B	B	14	15	17	600	150	9.0	2.3	0.3	.05	14	.21	.81	1.4	5.0	.94	4.8	55	7.9	35	2.1
262B	T	58	85	88	1900	4300	24	490	5.4	.78	165	1.5	1.7	9.1	7.5	1.1	7.0	49	6.5	2600	12
262C	T	89	138	147	3000	8000	36	920	11	1.31	285	2.0	2.3	16	9.0	2.4	9.7	47	6.1	1600	22
258A	T	73	64	44	1000	790	33	110	3.9	.51	90	1.8	1.7	9.5	11	1.1	27.2	28	5.3	187	9.6
258B	T	60	83	48	1300	890	35	120	2.6	.34	100	2.6	1.9	11	10	1.3	28.9	26	7.7	78	9.8
258C	T	84	105	61	1500	1400	32	180	5.4	.58	115	2.5	2.4	10	13	1.6	23.1	32	6.0	81	16
259A	T	30	45	28	930	500	16	73	1.3	.13	60	.65	.97	5.5	8.0	.98	7.4	72	6.9	74	5.3
259A	B	21	19	19	740	180	23	23	.65	.06	30	.83	.83	3.4	2.0	.80	6.1	85	8.0	44	3.2
259B	T	39	63	35	1300	870	18	110	2.1	.20	64	.90	1.2	5.0	8.5	1.2	7.9	63	5.3	210	7.0
259B	B	19	17	18	780	160	13	19	.5	.06	50	.42	.61	4.0	4.0	.66	6.6	150	7.3	18	2.7
259C	T	46	84	44	1500	1400	24	180	3.0	.3	83	1.2	1.5	5.7	9.5	1.3	8.5	53	6.3	258	9.4
259C	B	21	23	23	830	200	16	26	0.3	.08	27	.42	.85	2.8	5.0	.78	7.4	83	7.4	<18	4.1
254	T	81	170	67	1700	2400	36	300	6.0	.52	137	1.6	1.7	9.4	10	1.6	10.0	47	8.1	443	17

Table A-3 continued

Station No.	Top or Bottom Portion	Cu	Cr	Fe*	Mn	Zn	Ni	Pb	Cd	Hg	COD*	TKN*	Total P	LOI(%)	Co	Acid Extractable P*	Al*	Ca*	Mg*	Sulfide	As
254B	B	22	21	20	550	140	14	15	0.3	.04	82	1.5	.77	6.4	7.5	.68	7.8	65	7.7	<18	4.0
255	T	62	80	30	730	450	22	74	2.0	.27	60	.95	1.2	4.4	6.0	.76	6.1	100	6.5	44	7.4
256A	T	100	262	82	1600	2000	36	220	4.5	.79	135	2.5	2.4	9.3	8.0	1.6	8.7	97	6.8	259	19
256A	T**	98	290	82	1400	3800	51	640	8.6	.66	110	2.1	2.1	8.5	6.2	1.4	7.4	81	6.1	388	14
256A	B	62	134	29	550	480	21	82	3.0	.27	123	2.8	1.3	8.8	4.5	1.0	5.9	180	4.8	<18	6.5
256B	T	100	330	87	1560	2600	39	460	8.0	.87	130	2.3	2.3	9.1	6.0	1.4	8.8	80	7.4	270	17
256B	B	50	116	23	480	370	20	64	2.5	.28	115	2.8	1.3	8.4	6.0	1.0	5.2	180	4.6	44	6.2
256C	T	91	330	85	1500	4400	34	590	8.5	.52	110	1.79	2.3	8.1	10	1.6	9.9	83	7.4	272	15
256C	B	58	117	27	520	430	19	71	2.0	.27	110	2.8	1.3	8.4	4.5	0.90	2.5	170	4.9	<18	6.0
2	T	350	1125	441	3200	2100	190	370	1.5	.75	360	1.7	1.7	13	22	1.1	2.5	20	1.7	163	42
268	T	38	82	19	510	410	42.0	78	2.0	.11	80	1.8	1.8	61	8.0	1.5	6.1	57	6.2	137	3.6
268	B	37	45	24	650	470	20	66	0.5	0.1	120	3.4	1.0	9.1	6.0	9.0	9.0	95	6.5	33	5.6
20A	T	56	100	37	970	840	23	100	2.4	.38	85	1.8	1.8	6.1	2.0	1.6	6.4	32	5.7	170	10
20A	B	18	7.5	11	510	96	5.5	4.0	2.0	.05	30	.8	.63	2.9	4.0	.34	3.4	65	1.3	<18	2.2
20B	T	72	145	46	1080	1200	21	140	3.2	.4	105	1.8	2.1	8.1	7.0	1.8	6.8	110	5.9	237	11
20B	B	20	20	15	610	200	7.5	19	0.3	0.1	30	1.2	.95	3.2	4.0	0.5	4.0	88	4.3	30	13
20C	T	58	112	39	1100	960	19	130	2.0	.37	87	1.6	1.9	6.7	5.0	1.5	2.5	110	5.1	163	9.8
267	T	61	115	39	1000	835	23	110	1.5	.27	120	1.6	1.7	7.2	6.5	1.3	6.4	82	4.9	192	13
4	T	100	240	71	1600	2600	35	360	6.0	.38	102	1.6	2.4	9.2	9.0	1.7	9.9	53	4.6	340	18
4	B	30	12	16	770	94	10	5.0	0.3	.03	14	.22	.66	1.8	5.0	.52	5.2	91	3.8	<18	2/7

Note: * These results are in mg/g. All other results are in $\mu\text{g/g}$, unless otherwise stated.
 ** Layer approximately 20-45 cm from sediment-water interface, classified at top because its characteristics were very similar to 256B and 256C tops.

HAMILTON HARBOUR STUDY '75

section D

Methane Production
and Oxidation

GAS PRODUCTION BY THE SEDIMENTS: AN OXYGEN SINK

SUMMARY

SAMPLES OF GAS GENERATED BY HAMILTON HARBOUR SEDIMENTS WERE COLLECTED AT THE TOP AND BOTTOM OF THE WATER COLUMN AT TWO STATIONS (IN 1975). METHANE AND NITROGEN WERE THE ONLY SIGNIFICANT GASES PRESENT. A LITERATURE REVIEW INDICATED THAT METHANE RESULTED FROM THE ANAEROBIC FERMENTATION OF ORGANIC MATTER IN THE SEDIMENTS, NITROGEN RESULTED FROM THE NITRIFICATION OF AMMONIA (AN OXIC PROCESS) AND SUBSEQUENT DENITRIFICATION OF NITRATE (AN ANOXIC PROCESS). APPROXIMATELY FIFTY PERCENT OF METHANE WAS LOST FROM THE RISING BUBBLES, BUT NITROGEN WAS NOT LOST. THE METHANE PRODUCTION RATE WAS HIGHER AT A STATION CLOSE TO THE WASTEWATER TREATMENT PLANT OUTFALLS (STATION 4) THAN AT A STATION FURTHER AWAY (STATION 270). SUCH PRODUCTION REPRESENTED A SELF-REGULATORY APPROACH FOR A BODY OF WATER TO PREVENT EXCESSIVE BUILDUP OF CARBON IN ITS SEDIMENTS. COMPLETE OXIDATION OF METHANE LOST FROM RISING GAS BUBBLES REPRESENTED AN OXYGEN SINK OF $0.3 \text{ g O}_2 \text{ m}^{-2} \text{ DAY}^{-1}$; NITROGEN PRODUCTION REPRESENTED AN OXYGEN SINK OF $0.1 \text{ g O}_2 \text{ m}^{-2} \text{ DAY}^{-1}$, ASSUMING NITRIFICATION-DENITRIFICATION OF AMMONIA. COMPARISON WITH ESTIMATES OF THE HYPOLIMNETIC OXYGEN DEMAND AND ESTIMATES OF INPUTS FROM LAND-BASED SOURCES SUGGESTED THAT METHANE AND NITROGEN PRODUCTION REPRESENTED SIGNIFICANT BUT SMALL PORTIONS OF THE TOTAL OXYGEN DEPLETIONS IN THE HARBOUR.

HAMILTON HARBOUR STUDY
GAS PRODUCTION BY THE SEDIMENTS:
AN OXYGEN SINK

The dominant water quality problem evidenced in Hamilton Harbour is the hypolimnetic oxygen demand which results in a rapid loss of oxygen from the hypolimnion after the onset of summer stratification (OME, 1974, 1975). This author characterizes the hypolimnetic oxygen demand to consist of four major components:

1. the biological sediment oxygen demand (due to bacterial respiration),
2. the chemical sediment oxygen demand (due to oxidation of reduced chemical species such as Fe^{2+} , H_2S , and NH_3),
3. oxic decomposition of organic material in the water column, and
4. methane oxidation in the water column.

The sediment oxygen demand components are both interfacial processes exerting an oxygen demand at the bottom of the water column; oxic decomposition and methane oxidation are processes which occur throughout the water column. To measure these components in 1975, this author examined the effects of gas production (CH_4 , N_2) on the oxygen regime in the Harbour. In cooperation with OME personnel, attempts were made to characterize the sediment oxygen demand. Late arrival of equipment (late fall) prevented adequate characterization of the sediment oxygen demand.

The objective of the 1975 surveys was three fold:

1. to monitor the gases produced by the sediments of Hamilton Harbour,
2. to determine the amount of the hypolimnetic oxygen demand which is due to such gas formation, and
3. to measure any effects which the artificial mixing would have on such gas production or the gaseous oxygen sink.

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Gas Production in Fresh-Water Bodies

(i) Methane Production

Methane production is an obligate anaerobic process consisting of two essential steps. The first step consists of the conversion of carbohydrates, fats and proteins to organic acids and alcohols by a bacterial group occasionally referred to as acid-formers; the second step involves conversion of the organic acids and alcohols to methane and carbon dioxide by a bacterial group which may be labelled as methane bacteria (for further amplification, see Foree and McCarty, 1970). In the sediments of natural systems, Berner (1971) considers that most methane production results from the fermentation of carbohydrates, but in systems where humic acids and other refractory organic materials predominate, methane can be produced but at slower rates.

Various investigators have made measurements related to methane production and consumption in lakes. Hayward (1968) trapped gases at the sediments; Howard et al (1971) trapped gases and made a few measurements of the rate of methane utilization; Rudd (1974) made measurements of the concentration of dissolved methane and rate of methane oxidation; Jannasch (1975) observed methane formation in the deep waters and subsequent oxidation in the intermediate depths. Rudd's work is the most thorough and comprehensive, but all these works are reviewed here, in order to contrast their respective approaches.

Hayward (1968) observed in situ methane production of $0.22 \text{ gm CH}_4\text{m}^{-2}\text{day}^{-1}$ (coefficient of variation of 0.21) during June and of $0.48 \text{ gm CH}_4\text{m}^{-2}\text{day}^{-1}$ in August from the sediments of University Lake, North Carolina, a small eutrophic lake used for water supply. The collector, located a few inches above the bottom sediments, was coupled by a plastic tube running from the collector to a sample bottle at the water surface. Daily samples were taken from the sample bottle. The author thinks this technique under-estimates the total methane produced by the sediments¹. Since problems existed with a surface sampler, no statements can be made about the amount of methane lost from rising gas bubbles to the water column².

Howard et al (1971) studied the rate of methane oxidation at three near shore locations in the western basin of Lake Erie. Samples were collected from different depths; 80 ml bottles were filled with sample water and CH_4 gas, and the rate of decrease of dissolved CH_4 was monitored. Their calculations indicate methane depletion rates of approximately

^{1, 2} Please see Appendix for comment.

0.04 mg CH₄ l⁻¹ day⁻¹ at 25°C. The incubation temperatures were higher than in situ temperatures. Also, epoxy coated, inverted funnels were placed 15 cm above the sediments. Rates of gas evolution were determined for a variety of time periods (10 min-5 days) and found to be independent of length of sampling period. Above a sediment bottom area, the gas was 95% methane, 3% nitrogen and 2% carbon dioxide and the gas evolution rate was 1.6 gm CH₄ m⁻² day⁻¹, but above an area devoid of sediments, no production was observed. At the location with the sediment bottom, dissolved methane was generally found throughout the water column, but methane oxidation occurred primarily in the bottom half of the water column. The dissolved methane concentrations found throughout the water column are consistent with the hypothesis that bubbles of methane gas are escaping to the atmosphere; however the absence of a surface collector prevents complete confirmation of this hypothesis.

Rudd et al (1974) used a radiotracer method to measure the rate of conversion of dissolved CH₄ to cell material and CO₂ on lakes near Kenora, Ontario (Experimental Lakes Area). The author considers this method to be superior to Howard's. The method consists of pumping water from different depths, putting the sample in the sample bottle, bringing it to the lab, spiking it with a small amount of radioactive ¹⁴CH₄ and measuring the conversion of ¹⁴CH₄ to ¹⁴CO₂ and ¹⁴C biomass after a certain time period. They found a peak oxidation rate of 0.4 mg CH₄ l⁻¹ day⁻¹ for an eutrophic lake but 0.06 mg CH₄ l⁻¹ day⁻¹ for a meromictic lake. Of this oxidation rate, approximately one-third of the methane was converted to cell material and two-thirds was oxidized to CO₂. Generally, most oxidation occurred in a two meter lens of water which straddled the transition zone of oxic-anoxic conditions in the hypolimnion. Above and below this lens, methane oxidation rates were negligible. A characteristic profile is shown in Figure 1. Assuming that all significant methane oxidation occurred in this 2-m lens, this represents an oxygen consumption rate* of 1 gm O₂ m⁻² day⁻¹** for the eutrophic lake but 0.15 gm O₂ m⁻² day⁻¹** for the meromictic lake.

It is significant that negligible amounts of methane were observed by Rudd et al in the top part of their lakes. While they did not put a gas collector at the top of the water column, such insignificant amounts of dissolved methane suggest that no gaseous methane would escape out of the lake.

*

All oxygen consumption calculations presented herein are made by this writer and are based upon assuming the reaction CH₄ + 2O₂ → CO₂ + 2H₂O.

**

This assumes conversion of 2/3 of CH₄ to CO₂ and a zero oxidation rate at the top and bottom of the lens.

Rudd and Hamilton (1975) assessed the influence of methane concentration, temperature, oxygen concentration and pH on the methane oxidation rate. They found that the primary controlling variable is the oxygen concentration (the optimum range is 0.1 to 1.0 mg O₂l⁻¹) and thermal stratification. Concentrations in excess of 1 mg O₂l⁻¹ inhibited methane oxidation. Recent work (Rudd, personal comm.) suggests that nitrate concentrations also control the methane oxidation rate. This control predominates over oxygen concentration since high methane oxidation rates are observed during fall and early winter, a period when oxygen concentrations are high. An explanation for nitrate control awaits further assessment. Analogously, it is expected that high methane oxidation rates would be found throughout the water column of Hamilton Harbor, since the nitrate concentrations are sufficient to cause high methane oxidation rates.

Jannasch (1975) found methane oxidation rates of '0.48 mmoles m⁻³day⁻¹' in Lake Kivu (a 460m deep lake in the rift valley of Central Africa). The lake is permanently stratified. Below a depth of 50m, the lake remains anoxic and hence provides no potential for methane oxidation; above 35m, little dissolved methane is found. Thus Jannasch concludes that the effective layer of methane oxidation occurs between 35m and 50m. In the anoxic stratified waters, step increases in the methane concentration gradient with depth are observed, coinciding with stepwise decreases of other chemical species - these steps represent layers of water well mixed within themselves, but separated from one another by sharp boundaries. To measure oxidation rates, Jannasch obtained samples of water from different depths and incubated them in the laboratory for a period of days. Methane concentrations were measured every few days until the samples went anoxic. These measurements permitted estimation of the rate of methane oxidation (assuming that conversion of CH₄ to CO₂ was complete). In fact, their measurements represent the rate of loss of dissolved methane; estimates for oxygen consumption represents an upper limit since Rudd et al's work suggest that some methane is converted into biomass.

Assuming complete microbial oxidation, their observed methane oxidation rate (7.2 mmoles m⁻²day⁻¹) represents an oxygen consumption rate of 0.46 gm O₂m⁻²day⁻¹. This rate of methane oxidation is similar to that of Rudd et al (1974) whose variable rates can be explained by seasonal variations of methane production and higher methane concentrations. By comparison, Jannasch observes that the oxidation rates of Lake Kivu are not interrupted by such seasonal changes. Methane production rates are estimated by Jannasch to be similar to the oxidation rates*. Such production provides

* This author observes however that lack of precise, direct measurements preclude statements of whether the methane stocks are increasing or decreasing.

evidence for the hypothesis of Jannasch's co-workers that the observed increase in temperature of the deep waters over the last 35 years could be attributed to the release of energy during methane formation in the deep water.

For the winter period of 1974 in Lake 227 (under ice cover), the data of Rudd and Hamilton (1975) indicate that the complete oxidation of CH_4 to CO_2 consumed oxygen at the rate of $0.18 \text{ gm m}^{-2}\text{day}^{-1}$ *. For the same time period and under ice, the oxygen depletion rate for the whole lake was $0.2 \text{ gm m}^{-2}\text{day}^{-1}$ ** . These calculations indicate that for this period, the oxygen depletion rate under ice can be explained almost wholly by oxidation of methane to carbon dioxide. Methane oxidation rates observed by Rudd and Hamilton were as high during the spring as the winter period but much lower during the summer. Hence for summer conditions, the exact portion of the hypolimnetic oxygen depletion rate represented by methane oxidation awaits further assessment.

(ii) Nitrogen Production

Nitrogen formation results from the reduction of nitrates by bacteria (e.g. pseudomonas). This process, called denitrification, uses nitrate as the terminal electron acceptor and several enzyme-mediated intermediate steps before N_2 is formed (Brezonik, 1975). Denitrification is essentially an anaerobic process; it can occur in the presence of trace amounts of oxygen, only if the micro-organisms are metabolizing in an anoxic microzone. Some authors report that denitrification proceeds in an oxygenated culture (e.g. Jannasch, 1960); however, Brezonik concludes that denitrification would occur (in such cultures) if a micro-anoxic zone surrounded the bacterial cell or organic particle. Other investigators (e.g., Painter, 1970) have reported that nitrite can be aerobically reduced to N_2 , but Brezonik concludes that such denitrification would be small. Of the several possible pathways proposed for denitrification, all regard the essential steps as being,

Oxidation State	+5	+3	+2	+1	0
Reaction Steps	$\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2\uparrow$.				

* (This calculation by this investigator is based on the average of measurements of "moles CH_4 oxidized in the whole lake per day" made at 5 different times by Rudd for the Jan.-Mar. 1974 period, and assumes that two-thirds of the CH_4 oxidized to CO_2).

** (Analysis of the decrease in stocks of oxygen under ice over time. This assumes that replenishment of O_2 due to reaeration of influent streams is negligible. Data for oxygen stocks was furnished by D.W. Schlindler).

Some controversy exists as to whether or not N_2O solely (e.g., Cox and Payne, 1973) or N_2O together with NOH and $N_2O_2^{-2}$ (Painter, 1970) results from the third step.

Since denitrification occurs under anoxic conditions, the source of nitrate may be one of two sources, "stripping of nitrate from the overlying water" (diffusion of nitrate from the overlying water to the denitrification sites) or via nitrification. Nitrification is the process by which organic nitrogen or ammonia is oxidized to nitrate. Nitrification involves two essential steps, oxidation of ammonia to nitrate (by Nitrosomonas) and oxidation of nitrite to nitrate (by Nitrobacter). As oxygen is the electron donor, nitrification is an oxic process. (for the microbiology of nitrification, see Painter, 1970). The ammonia is formed by the anaerobic decomposition of organic matter. For the ammonia to be utilized in nitrification, it must diffuse out of the anoxic zone into the oxic sediment zone.

Thus to assess gaseous nitrogen formation, the following question arises - which is the more probable pathway for N_2 (gas) formation, (i) diffusion of nitrate down from the overlying water past an oxic nitrification site to the anoxic denitrification site (nitrate stripping), (ii) diffusion of ammonia up from the anoxic sediments past an anoxic denitrification site to an oxic nitrification site and subsequent diffusion of the nitrate back down to a denitrification site or (iii) diffusion of ammonia down from the overlying water to a nitrification-denitrification site. All pathways are possible in Hamilton Harbor. Ammonia is formed by anoxic sediments; diffusion (due to mixing of sediments) should be sufficient to cause its upward transport. The nitrate concentrations are sufficiently high to allow downward diffusion of nitrate.

At this time, this work considers that nitrification-denitrification is probably the dominant mechanism for N_2 formation. This does not preclude the importance of nitrate stripping from the overlying water. Keeney (1972) notes that Greenwood (1962), Patnaik (1965) and Chen et al (1972) have observed that nitrification and denitrification occur simultaneously in a system. Patnaik added a $^{15}NH_4$ isotope to a soil; nitrification occurred in the oxidized surface layer and subsequent denitrification occurred in the reduced zone. Chen et al observed both processes occurring in lake sediments which were incubated under an air atmosphere in the laboratory. Greenwood's work is somewhat less conclusive than as described by Keeney - under quiescent conditions for lake sediments, ammonia decreased but much less nitrate accumulated. This indicates that nitrate was produced in the upper sediment by nitrification but nitrate reduction could occur either by denitrification or by nitrate reduction by organic matter - denitrification is most probable but not assured. Chen et al in other laboratory experiments (when $^{15}NO_3$ was added to lake sediments) observed both ^{15}N in the atmosphere above

the Lake Mendota sediment samples and in the organic-N and ammonium fractions. In a field experiment, Keeney et al (1971) found that after 4 days, 37% of $^{15}\text{NO}_3^-$ added to sediment samples was converted to organic-N and ammonium and 63% was denitrified.

Kamp-Neilsen and Andersen (1975) reviewed the process of ammonia formation from organic material in the sediments, nitrification and subsequent denitrification. For one lake biological ammonification is the rate limiting step with a temperature dependent release whose Q_{10} is 2. For another lake, the seasonal variation is described by variations in sedimentation, temperature and redox conditions. The nitrification rate is controlled by oxygen concentration and ammonia or nitrite concentration; but the denitrification rate is controlled by the nitrate concentration. These observations lead them to suggest that either the rate of transport of nitrate into the sediment or the rate of formation of nitrate in the sediment is the rate determining step. They also note that Andersen (1974) has proposed a nitrification-denitrification mechanism for shallow lakes if sediment stirring occurs. Nitrification occurs when the stirring causes the anoxic sediments to become suspended and the nitrate is subsequently denitrified when respiration and nitrification consumes all the oxygen in the same sediment stratum. Such a mechanism would provide for N_2 formation, without using any nitrate whose source is via diffusion from the overlying water to the anoxic layer.

Larsen (1975) observed the processes of ammonification, nitrification, nitrate assimilation and denitrification in 5 Danish lakes, whose hypolimnetic waters become anoxic during summer stratification. All processes were observed to occur in the hypolimnetic waters. As the temperature increased from 3°C to 6.5°C , the ammonia content increased and subsequent nitrification occurred. A maximum nitrate concentration was observed in the summer when nitrification ceased. Cessation of hypolimnetic nitrification was probably due to the decrease of dissolved oxygen concentration to a value prohibitive to nitrification ($1.5 \text{ O}_2 \text{ mg/l}$)*. Nitrate removal was observed to occur by two mechanisms-nitrate reduction (conversion to organic particulate forms) and denitrification. For all 5 lakes, nitrate reduction accounted for 5-95% of the total nitrate removal. With the exception of one lake, hypolimnetic nitrate was completely removed; for this exception, the anaerobic period appeared to be sufficiently short to prevent complete nitrate removal. Denitrification was also

* Larsen did not assess nitrification in the water column, but it is probable that nitrification would continue in the oxic-anoxic transition zone in the water column - this would assure continued formation of nitrate. Slow vertical transport of ammonia up to oxygenated water may prevent this from being a significant mechanism.

observed on the lake sediments. Of nitrate removal observed, approximately 60% was by denitrification and 30-40% was by reduction to NH_3 .

A nitrogen budget was estimated for 2 lakes. For a lake whose mean depth was 10m, 92% of the total denitrification occurred in the sediments but for a lake whose mean depth was 14m, 40% of the total denitrification occurred in the sediments. Such data lead Larsen to conclude that in deep lakes, the free water 'might be' more important than the sediments as a denitrification location. This conclusion is reasonable, but the difference of mean depth of these two lakes (10m vs 14m) does not justify such a conclusion. Furthermore, this writer asserts that the high percentage of denitrification in the sediments of the 10m lake is unreasonable. Sustained denitrification depends upon a continuous nitrate source. When the hypolimnetic waters become anoxic and the nitrate in the sediments is used up, denitrification cannot proceed. The hypolimnion of both the 10m and the 14m lakes became anoxic. Hence the low amount of sediment denitrification in the 14m lake is appropriate. The high percentage of sediment denitrification in the 10m lake would require the presence of a large reserve of nitrate in the sediments to sustain denitrification. Since nitrate disappeared from the adjoining, overlying anoxic water halfway through the stratification period, such a reserve appears to be high, as does the large percentage of denitrification attributed to the sediments³.

Barnes et al (1975) made measurements of $\text{N}_2:\text{Ar}$ concentration ratios and of nitrate and nitrite in the pore waters of sediments in an ocean trench off Southern California. The depth of water (3000m) prevented formation of gas bubbles. With sediment depth, the NO_3^- gradient decreases and the N_2 gradient increases. Their calculations indicate, that of the total N_2 that would be lost from the sediments by diffusion, only approximately 20% of its formation can be explained by denitrification of nitrate which would diffuse into the sediments - the remainder would come from some other source. They conclude that the source is the ammonium ion, released by sediment degradation of organic nitrogen compounds. Further, they postulate that the conversion of NH_4^+ to N_2 is through a NO_2^- (nitrite) intermediate under conditions of low oxygen tension. Their postulate is based upon the work of other investigators who have demonstrated the bacterial oxidation of ammonia to nitrite. This work conflicts with our postulate that the conversion goes from $\text{NH}_4 \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$ under oxic conditions and then $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$ in an anoxic microzone, consistent with the pathways described above for nitrification-denitrification.

Vanderborght and Beller (1975) observed the nitrite and nitrate profiles in the interstitial water of marine sediments of a small lagoon. Analysis of the profiles together with formulation of an one-dimensional model describing nitrification,

denitrification, diffusion and sedimentation showed reasonable agreement with measured profiles. For a "muddy" type of sediment, in which nitrate concentration in the pore water was lower than in the overlying water, a model incorporating denitrification, diffusion and sedimentation described the profile. For a sandy soil, in which the nitrate concentrations in the interstitial water of the top sediment layers were higher than the nitrate concentrations in the overlying water, a model incorporating nitrification in the top few centimeters and denitrification below this depth together with diffusion through the sediments and sedimentation described the profiles. This depth was chosen because, at greater depths, the value of E_h fell below the value for which the oxidation of ammonium was no longer exoenergetic (approximately 200-250 m V). Since measurements were not made of N_2 and NH_3 profiles nor of nitrification in the water overlying the strongly reducing muddy sediments, model predictions of these factors were not attempted. This represents an area for further refinement of their work. But their results provide a perspective for differentiation of sediments: sufficiently well-packed sediments would prevent penetration of oxygen, and would be sufficiently anoxic to prevent nitrification; for such sediments, nitrification would occur only in the overlying water.

Methods of Collection and Analysis

A gas trap in the shape of an inverted cone (base cross-sectional area 0.1 m^2) has been constructed for sampling gases (see Figure 2). The assembly consists of a copper, one liter sample bottle closed by a $\frac{1}{2}$ inch gate valve. The conical portion is fastened to three legs, each connected to a $0.1 \text{ m} \times 0.1 \text{ m}$ metal pad to prevent the sampler from sinking into the sediments. Each sample bottle is pressure tested to 25 psi to ensure the joints. The base of the conical funnel is 0.15 m above the sediments and a minimum of 0.23 m from the inside edge of the pad. This arrangement prevents isolation of the sediments below the sampler while minimizing the disturbance of the projected area of the cone on the sediments. This arrangement was strongly influenced by Hayward's (1968) work. Differences in gases collected by samplers at the top and bottom of the water column are taken to represent the amount of methane oxidized. While the method of Rudd et al (1974) is more precise, its complexity and the length of time required to master the technique precluded its use in 1975.

To measure gas lost in the water column, gas samplers are placed at the top and bottom of the water column (see Figure 5). For station 4, a top sampler and bottom sampler were maintained from July to December. For station 270, four top samplers and four bottom samplers were inserted in October; loss of sample bottles and two samplers during November make the November data somewhat limited. The top samplers are attached to the marker spar, while the bottom samplers are

positioned between 30 and 60 m from the marker-spar. The exact distance varies, depending upon winds and currents but each bottom sampler is maintained in approximately the same location. At station 4, the bottom sampler is inserted east of the spar; at station 270, the bottom samplers are inserted at approximately the north (N), south (S), east (E), and west (W) compass points from the spar. Thus the bottom collectors sample an area described by a radius of 30-60 m from the marker-spar while the top collectors sample an area described by an 8 m radius.

The top sampler is supported by a surface float (collar buoy) such that gas was collected at the 1.3 m depth; the bottom sampler, sitting on the sediments is connected by a rope to a surface marker buoy. As gas bubbles rise from the sediments or through the water column, they enter the funnel and rise into the sample bottle, displacing an equal volume of water. To collect the accumulated gases, the sampler is pulled to the side of the boat, the valve on the sample bottle is closed while the bottom part of the funnel is still in the water (to prevent atmospheric invasion of the sample bottle) and the sampler is lifted into the boat. The sample bottle is removed, a new sample bottle full of water is attached to the sampler in an inverted position, the valve on the sample bottle is opened, and then the upside down assembly is resubmerged. When it is certain that no air bubbles remain in the cone, the sampler is allowed to assume an upright position, and then to go to its sampling position. For the bottom sampler, care is taken to ensure that it is in an upright position when it comes to rest on the sediments by raising sampler from the bottom about 0.5m then lowering it into position.

The sample bottles (with a water seal to prevent the gas from diffusing through the closed valve) are transported to the laboratory; the volumes collected are measured and analyzed for composition. The gas analysis is performed on a Gas Partitioner (Fisher Model 25) equipped with a 30 inch silica gel column followed by a 5 foot molecular sieve 5A column using helium as a carrier gas at the rate of 40 ml/min. The detector is a thermal couple using a tungston element and this arrangement separates the 0.5 ml gas sample into CO_2 , O_2 , N_2 and CH_4 in that order. Calibration with peak height is made with known standards.

Analysis and Conclusions from Gas Production Data

A summary of gas collection is shown in Tables 1 to 3 and Figures 3 and 4 for Stations 4 and 270. As a function of time, the average rates of gas production, of methane production, and of nitrogen production, and average percent of methane and of nitrogen in the gas bubble are shown in Figure 3 for station 4, and in Figure 4 for station 270. The significance of the differences of top and bottom samples

is assessed using the paracentric one-tailed "t" test. Use of the t test assumes that the samples are drawn from a normal distribution and that successive observations are stationary (i.e., time independent).

Examination of Figures 3 and 4 suggest stationary conditions (not a function of time) which are similar to the findings of Howard et al (1971). For the volumetric, methane and nitrogen production rates and the percentage of methane, the hypothesis tested is that the bottom sample is greater than the top sample; for the percentage of nitrogen, the hypothesis tested is that the top sample is greater than the bottom sample. In Table 3, the hypothesis that production of the sediments at station 4 is greater than production at station 270 is tested for all gas production parameters.

Only data before November 3 were used. This corresponds to the beginning of the period when several sample bottles and samplers were lost at #270, to the start of sustained colder conditions of the late fall, and to a period when a few of the bottom samplers collected negligible amounts of gas.

Based upon these analyses, the following statements are made:

1. Methane and nitrogen are the only gases which are consistently collected in significant amounts. Occasional amounts of oxygen were obtained at the surface of station 270; only trace amounts (attributable to an air bubble in the sample cone before insertion into the water) of oxygen were observed in the bottom samples. No gaseous carbon dioxide (which might result from respiration) was ever observed*.
2. To test for oxidation of the gaseous CH_4 in the sample bottles in between collection times, the gas composition of several samples was monitored for one to two weeks in the laboratory. No significant change in composition was observed. This is taken as evidence that no significant oxidation of the gaseous methane which is trapped in the sample bottles occurs in situ before the bottles are collected.
3. The rate of methane production and percentage of methane in the gas is consistently higher in the bottom samples than the top samples over the time period of measurements (see Figures 3 and 4). Differences between top and bottom are small for the rate of nitrogen production.
4. There is no apparent temporal trend in gas production - this suggests that the data are stationary.

* Some oxygen production is expected at the surface because of entrapment of photosynthesizing algae in the sample bottle. Any CO_2 produced by respiration probably reacts with H_2O to form carbonic acid, precluding formation of gaseous CO_2 .

5. At the 5% level of significance, the volume rate of production, methane production rate and percentage methane in the gas collected is significantly higher at the bottom than at the top. The percentage nitrogen is significantly lower at the bottom than at the top, but the nitrogen production rates at the top and bottom are not significantly different. These differences are the same for both station 4 and station 270.
6. These data support the conclusion that as a gas bubble rises from the sediments, methane will be lost into the water, where it undergoes oxidation (the rate of methane collected decreases from top to bottom, the percentage of methane decreases) but nitrogen will be conservative (the rate of nitrogen collected at the bottom and top remains the same). The increase of nitrogen in a gas bubble as it rises from bottom to top is due to the loss of methane from the bubble. The decrease in total volume of gas collected between bottom and top is due to the loss of methane from the gas bubbles.
7. For the sediments, the volume production rate, methane production rate and percentage of methane in the gas are significantly higher at station 4 than that at station 270. The percentage of nitrogen is significantly higher at station 270 than at station 4, but there is no significant difference in nitrogen production rates (see Table 3). These data support the conclusion that the methane production rate is higher at station 4 (the station close to various municipal and industrial discharges) than at station 270 (a station more removed from such influences).
8. 52% of the methane is lost from the gas at station 4 (the 21 m station); 56% of the methane is lost from the gas at station 270 (the 10 m station). These differences do not appear significant. However, twice as much methane is lost in the water column at station 4 as at station 270 ($80 \text{ mg/m}^{-2}\text{day}^{-1}$ vs $40 \text{ mg/m}^{-2}\text{day}^{-1}$). The depth of station 4 is twice that of station 270. In a deeper water column, it is expected that more methane oxidation and hence greater methane loss would occur than at a shallower station. Hence it is expected that both the percentage of methane lost and mass of methane lost would be larger in deeper water. The effect of water depth on methane loss awaits further assessment.

Relationship of Gas Production to the Hypolimnion Oxygen Regime

(i) Estimates of Hypolimnetic Depletion Rate

The depth-temperature profiles for the period June 21 to 26 are stable and have large gradients indicating little vertical

transport of O_2 between epilimnion and hypolimnion. During this period, a rapid loss of oxygen from the hypolimnetic waters occurs at stations 4, 258, and 270. During other periods in the spring and early summer, the temperature gradient is more diffuse, indicating conditions conducive to vertical transport of oxygen from the epilimnion to the hypolimnion. With a sharp temperature gradient, the rate of oxygen loss may be used as an estimate of the hypolimnetic oxygen demand. This will be a conservative estimate since some vertical transport would add some oxygen to the hypolimnion. For this period, the hypolimnetic oxygen demand (see Table 5 (a)) is estimated to range from 1 to 4 (mean 2.2) $gm\ O_2 m^{-2} day^{-1}$. This demand is due to the combined effects of water column demands (e.g. methane oxidation, net decomposition of organic matter) and sediment oxygen demands (e.g. biological, and chemical including nitrification-denitrification, Fe^{2+} and H_2S oxidation).

Another method for assessing the oxygen demand is presented in Table 5 (b). There, the rate of decrease in oxygen stocks during the spring of 1972 is assessed as representing harbour oxygen demand of 0f $0.8\ gm\ O_2 m^{-2}\ day^{-1}$. (Data on O_2 stocks are from OME, 1974). Since the oxygen stocks are always less than the equivalent saturated value, net transport always act to add oxygen from the atmosphere to the water; hence, the loss is due only to sediment and water column demands. This harbour oxygen demand represents an underestimate of the hypolimnetic oxygen demand, (i) Since the O_2 stocks include epilimnetic oxygen which remains approximately constant (hence the actual rate of hypolimnetic oxygen demand is higher) and (II) since reaeration and inflows of oxygen rich water from Lake Ontario act to replenish the oxygen stocks. Further, actual use of 1972 data must be viewed with circumspection because of the paucity of O_2 data collected during 1972. This work concludes that a reasonable estimate for the hypolimnetic oxygen demand is $2\ gm\ O_2 m^{-2} day^{-1}$ for a mean hypolimnetic depth of 8m.

(ii) Estimates of Oxygen Demand of Land-Based Inputs

In Table 6, estimates of the potential oxygen demand due to wastewater inputs are made. Data were obtained from the OME and from the 1974 Hamilton WWTP report. For the harbour as a whole, this potential oxygen demand corresponds to an areal rate of $1.4\ gm\ m^{-2} day^{-1}$. However, this should be viewed with much caution for the following reasons: (i) This calculation assumes, that on an annual basis, all the BOD and ammonia oxidation is exerted. (ii) The BOD_5 represents an underestimate of the ultimate BOD (BOD_5 is usually about 70% of the ultimate BOD - if all BOD (ultimate) is exerted, the demand rate is higher). (iii) No evidence is available to describe the kinetics of BOD exertion - such evidence is necessary to accurately estimate the actual O_2 demand due to wastewater inputs. (iv) Much of the BOD_5 is particulate in nature. Such particulate material settles out and does not

exert a demand in the water column. (v) Much of the oxygen demand of the wastewater inputs is probably exerted in the Windemere Basin, in epilimnetic waters. Such an exertion is not a part of the hypolimnetic oxygen demand, although it is reasonable to expect that some of the wastewater inputs will reach the hypolimnetic waters. (vi) The BOD test is usually conducted using a seed of organisms acclimatized to the wastewater; organisms characteristic of the harbor may exert a slower rate of demand. (vii) The estimates for Table 5 do not include stormwater inputs which are expected to be low. Nevertheless, it is reasonable to conclude that the oxygen demand due to wastewater inputs may represent a significant part of the hypolimnetic oxygen demand.

(iii) Discussion

The average rate of methane loss ($81 \text{ mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$) at station 4 represents an oxygen consumption rate of $0.32 \text{ gm O}_2 \text{ m}^{-2} \text{ day}^{-1}$; the rate of nitrogen production at station 4 ($85 \text{ mg N}_2 \text{ m}^{-2} \text{ day}^{-1}$) represents an oxygen consumption rate of $0.14 \text{ gm O}_2 \text{ m}^{-2} \text{ day}^{-1}$. This assumes that the methane lost from the gas bubble is completely oxidized, and that the nitrogen production rate is due to nitrification-denitrification of ammonia produced in the anoxic zone of the sediments (according to $2\text{NH}_3 + 3/2 \text{ O}_2 \rightarrow \text{N}_2 \uparrow + 3\text{H}_2\text{O}$). The former represents an oxygen demand in the water column, the latter represents part of the sediment oxygen demand. The nitrification-denitrification estimate represents a maximum rate of oxygen consumption. Nitrogen formation by nitrate stripping (see literature review) from the overlying water is also a source of N_2 . Such a source is expected in Hamilton Harbour, but the dominant source should be due to ammonia oxidation. The methane oxidation estimate may be an overestimate or an underestimate. Incorporation of methane into biomass provides for an overestimate; transport of dissolved methane from the sediments into the water column by diffusive processes represents an additional source of methane in the water column in addition to gas transfer from a bubble and thus provides for an underestimate. Transport by diffusive processes is the dominant source in the lakes assessed by Rudd et al (1974) and Jannasch (1975). Further, Rudd's data indicate that methane transport by diffusion, together with methane oxidation, could account for all of a lake's oxygen demand under ice cover. At this time, it is tentatively concluded that the oxidation rate due to methane loss probably represents an underestimation of the oxygen consumption due to methane oxidation. The exact amount of hypolimnetic oxygen loss due to methane oxidation requires assessment by a technique which can directly measure the oxidation of dissolved methane as a function of depth. Such a technique is more sophisticated than that utilized during 1975.

These oxygen demands due to methane oxidation and nitrification-denitrification respectively represent 15 to 30% and 7 to

14% of a hypolimnetic oxygen demand of 1 to 2 gm m⁻² day⁻¹. The lower estimate of hypolimnetic oxygen demand is included because under conditions of low O₂ concentration, some aerobic bacteria respire at a slower rate (i.e., have a lower O₂ demand rate). Such demands due to gas production represent a significant portion of the hypolimnetic oxygen demand. Further, for the deeper areas of the hypolimnion in which the oxygen concentration remains at 1 mg l⁻¹ during June and July, methane oxidation could be used to explain maintenance of this low O₂ level. Rudd et al (1974) found that for the summer time, the maximum rate of methane oxidation occurred in water whose dissolved oxygen concentration ranged between 0 and 1 mg l⁻¹ - at such concentrations, bacterial respiration is sharply reduced.

Comparison of this work with the literature indicates that differences in dissolved methane regimes exist between water bodies. Fairly oligotrophic lakes such as those of Rudd et al (1974) have high concentrations of dissolved methane in the waters adjacent to the hypolimnion, but no dissolved methane in the upper waters. Methane production occurs in the sediments, but no gaseous methane leaves the lake to the atmosphere. The lake of Jannasch (1975) which is permanently stratified is anoxic in the bottom waters. Methane production occurs in the anoxic water column (and presumably in the sediments) because of reduction of organic material in the water column; methane oxidation occurs above this zone near the oxic-anoxic interface. Jannasch's estimates indicate that methane production and oxidation are approximately in balance. Jannasch found no dissolved methane in the top waters, indicating that no gaseous methane escapes to the atmosphere, similar to Rudd's lake, which is much shallower. But for Hamilton Harbour, for at least part of Lake Erie (Howard et al, 1971) and University Lake (Hayward, 1968) methane gas escapes to the atmosphere. Production occurs in the sediments, and some of the methane passed through the water column. Such bodies of water are characteristically more productive but have mean depths which are similar to those of Rudd. Both Hamilton Harbour and Lake Erie receive heavy inputs of wastewater; University Lake is a head-water lake, used for water-supply, to which organic inputs from human sources is minimal (a few septic tanks). Such methane production is due to anaerobic breakdown of such materials as carbohydrates as well as fulvic acids and lignins (Berner, 1972). Such materials, particularly carbohydrates can originate (i) from organic matter in wastewater which settles to the sediments, (ii) from the sedimentation of dead algae, and (iii) from the input of eroded vegetation (e.g. leaves). The escape of methane from such water bodies together with marshes may be the source of methane (hydrocarbons) which Steinfield (1975) notes is necessary to balance his calculations concerning the atmospheric carbon balance.

For Hamilton Harbour, it is hypothesized that the main source

of such organic material in the sediments is the accumulation of organic matter from human inputs (industrial and municipal sources) over the past 30-50 years. As such, methane production represents the process by which the sediments 'burn themselves out' by oxidizing these materials. This process is not extremely fast. Such production means that oxygen demands due to methane production will continue for a fair time.

With respect to E_h conditions, methane production occurs under very low E_h conditions (less than 50-75 mV). Denitrification of NO_3^- to N_2 occurs at an E_h of approximately 200-250 mV. Such reduction does not need strictly anoxic conditions, only an anoxic microzone in the vicinity of the reduction reaction. In between these two E_h ranges, reduction of SO_4 to H_2S and of Fe^{3+} to Fe^{2+} occurred (see Stumm and Morgan, 1970). For such reductions to occur, one might expect that N_2 , Fe^{2+} , H_2S and CH_4 production would occur vertically one below the other. However, production of large quantities of gaseous methane acts to mix the sediments because of the rising gas bubbles. Entry of nitrogen into the methane bubble occurs either by gaseous nitrogen formation or by stripping of the supersaturated pore water (with respect to nitrogen) by the methane bubble. Such mixing should cause the E_h to be fairly uniform throughout this mixing depth, and the surface sediments to have a lower E_h than expected. Hence rising bubbles are a mechanism for disrupting any micro-oxidized layer which is established either naturally or by artificial mixing - below the sediment surface. These mechanisms causing methane and nitrogen formation and usage are summarized in Figure 5.

Whether or not such sediment E_h conditions are the cause of the low E_h conditions (~250-300) measured in the harbour by OME is unknown. Under oxygen concentrations of 1 mg l^{-1} and greater, the E_h should be 400 mV or more. Use of the NO_3^- - NO_2^- couple and the NO_2^- - NH_3 couple together with data concerning concentrations of NO_3^- , NO_2^- and NH_3 measured in the harbour water indicate that the E_h should be approximately 430 mV. Using the same instrument, the E_h measured in Lake Ontario by OME was about 400 mV; hence interferences may be present in the harbour water. But the E_h decreased with depth - this follows expected behavior. The cause of these low E_h conditions in oxic waters awaits further work.

With respect to artificial mixing, no effect of artificial mixing on the rate of gas production during 1975 is detectable, because of the fact that the first gas samples were collected during the July period in which sustained mixing occurred. One aim of artificial mixing is to create a stable oxidized microzone in the sediments. Disruption of this zone by rising gas bubbles will occur, making maintenance of the microzone difficult. Delineation of sediment areas

in which gas production is high together with assessing the effects of artificial mixing on the location of the microzone in the sediments of such areas will provide information on whether or not an oxidized microzone can be maintained.

Future Necessary Work

These surveys during the past year point out the following needed surveys for 1976:

1. Use a more sophisticated technique for measuring methane oxidation to confirm the exact amount of methane which is oxidized. This will characterize how much of the hypolimnetic oxygen demand is due to methane oxidation, and whether methane oxidation is uniform throughout the hypolimnion or occurs mainly in the bottom part.
2. Relate methane production to the organic content of the sediments. This will provide the cause and effect relationship for methane production, and provide information as to whether such production is attributable to particular types of sediment characteristics. Relate methane production to the rate of replenishment of dissolved methane taking the rise rate of the bubble and the rate of escape of methane from the bubble into account.
3. Assess the oxygen demand due to biological and chemical sediment oxygen demand.
4. Assess the oxygen demand due to the decomposition of organic matter and respiration in the water column.
5. Assess (i) the effect of gas production on the stability of the oxidized microzone, (ii) the effect of artificial mixing upon gas production, and (iii) whether the presence of trace metals in the sediments affects the rate of gas production.

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APPENDIX:COMMENTS

(1) Since the gas collection bottle is located at the top, the gas bubbles pass up the tube, allowing potential exchange of CH_4 between the bubble and water. This exchange should keep the tube-water saturated with respect to methane while dissolved methane is being oxidized. When all oxygen inside the tube is consumed, anoxic conditions result, preventing any further methane oxidation. At this stage, no further significant loss of CH_4 collected at the top would be the same as that collected at the bottom.

(2) During the spring time, the hypolimnetic oxygen demand is $1.2 \text{ gm m}^{-2} \text{ day}^{-1}$. Subsequent experiments indicated that 25% of this demand is due to biological decay in the water column. If it is assumed that 50% of the methane collected is oxidized in the water column, such oxidation represented an oxygen demand of 0.45 and $0.95 \text{ gm O}_2 \text{ m}^{-2} \text{ day}^{-1}$. Such estimates support the hypothesis that much of the hypolimnetic oxygen demand is due to methane oxidation.

(3) Hayward found that this gas was approximately 75% methane and approximately 25% a gas not observed on the gas chromatograph column (silica gel, a column sensitive to methane, carbon dioxide, nitrogen). Since the other gas had the characteristic air peak, he concludes that this represents sample contamination (samples were transported 5 miles to a laboratory), and hence that only CH_4 was produced by the sediments. This conclusion has some merit since the hypolimnion of University lake (4m deep) is generally anaerobic after May 1. Under such conditions it is expected that anoxia conditions would present the presence of nitrate (for denitrification and N_2 formation) near the sediments. Since the sampler is located on the bottom sediments, no nitrogen should be collected. But a silica gel column should be able to detect nitrogen and oxygen. Hence his conclusion is circumspect.

(4) The newness of this collector presents some questions concerning sampler error. The sediment collector is 10 cm (approx.) above the sediments. This permits bottom currents to continue movement below the funnel allowing the sediment surface to be exposed to natural chemical conditions of the overlying water. Placement of an obstacle in the pathway of water movement causes displacement of the streamlines as suggested by the sketch. This will produce some turbulence and a possibility of some sediment erosion, however, such erosion is expected to be small.

Due to the nature of the harbour sediments, the feet of collector will sink into the sediments. We occasionally have observed $\frac{1}{4}$ to $\frac{1}{2}$ cm of sediments on top of the collector feet after it is brought to the water surface. After placing on "highly organic ooze-type sediments in near shore areas (where the depth of sinking could be monitored visually), observations indicated that the feet had sank in 2-3 cm. Hence due to the lightness of the sampler and the general ease of retrieval from the sediment surface (a light tug is generally sufficient to commence lifting the sampler), it is our conclusion that the sampler will sink into the sediments to a maximum of 2 to 3 cm.

The location of the feet away from collection plane ensures that, even if the collector assembly moves due to drag exerted on the surface buoy, any gas release due to such sediment disturbance should not be trapped by the collector. These aspects of the collector design provide some insurance that the time nature of the data collected is natural.

The location of the aerator (far from station 4 and 270) and shortness of the aerator period ensures that aeration had no effect on the gas collection.

Care in placing the bottom collector (allowing it to come to rest, relifting 0.5m and then again allowing to come to rest) ensures that the collector is upright.

No attempts were made to ascertain the size distribution of gas bubbles released by the sediments as this requires the use of a diver, anti-coagulant for a hydrosol and spectrum-sizing equipment. Such work may, if deemed critical in the future, be more appropriately examined in the laboratory, using tubes.

The larger variability of gas collected by the bottom sampler compared to the top sampler suggests that there is a great spatial variability in sediment gas production, but water movements tend to smooth the variations out as bubbles rise to the top of the water column.

The surface collectors move laterally due to surface water movements; observations during very strong current conditions showed that they remained basically vertical, ensuring that the whole collector area is available for trapping rising gas bubbles.

TABLE 1

SUMMARY STATISTICS FOR STATION 4, JULY 5-NOV.2, 1975*

	Top of #4			Bottom of #4				df
	\bar{X}	S	n \neq	\bar{X}	S	n \neq	t**	
Volume Rate (ml m ⁻² day ⁻¹) (20°C, 1 at m)	188	49.2	9	316	170	14	2.18	21
Methane Rate (mg m ⁻² day ⁻¹)	76	24	9	157	84	14	2.81	21
Nitrogen Rate (mg m ⁻² day ⁻¹)	83	29	9	89	73	13	0.203	20
% Methane by Volume in Bubble	59.8	9.7	11	77.0	8.3	15	4.86	24
% Nitrogen by Volume in Bubble	39.0	8.9	11	22.7	8.1	15	4.53	24

* \bar{X} = mean, S = standard deviation, n = number of observations
df = degrees of freedom

**For $\alpha = .05$, $t_{20df}=1.725$, $t_{21df}=1.721$, $t_{24df}=1.711$

\neq The number of samples collected are not equal due to loss of collectors, failure to record volume of gas collected.

TABLE 2

SUMMARY STATISTICS FOR STATION 270, OCT.14-NOV., 2, 1975*

	Top of #270			Bottom of #270				df
	\bar{X}	S	n	\bar{X}	S	n	t**	
Volume Rate (ml m ⁻² day ⁻¹)	114	87	21	191	167	23	1.902	42
Methane Rate (mg m ⁻² day ⁻¹)	38	32	21	87	89	23	2.343	42
Nitrogen Rate (mg m ⁻² day ⁻¹)	57	40	21	68	44	23	.843	42
% Methane by Volume in Bubble	50.1	8.4	21	63.4	12.4	23	4.242	42
% Nitrogen by Volume in Bubble	45.0	5.9	21	35.4	11.6	23	3.425	42

* \bar{X} , s, n, df as defined in Table 1

**For $\alpha=.05$, $t_{42df}=1.684$

TABLE 3
SUMMARY STATISTICS COMPARING GAS PRODUCTION
AT BOTTOM OF STATION 4 TO BOTTOM OF
STATION 270

	Bottom 270 \bar{X}	Bottom #4 \bar{X}	t*	dt
Volume Rate (ml m ⁻² day ⁻¹)	191	316	2.194	35
Methane Rate (mg m ⁻² day ⁻¹)	87	157	2.334	35
Nitrogen Rate (mg m ⁻² day ⁻¹)	68	89	1.032	34
% Methane in Bubble	63.4	77.0	3.810	36
% Nitrogen in Bubble	35.4	22.7	3.664	36

* For $\alpha=.05$, $t_{34df}=1.692$, $t_{35df}=1.691$, $t_{36df}=1.690$

TABLE 4(a)
SAMPLING PERIODS AT STATION 4
DURING 1975

<u>Date</u>	<u>Time Period</u>
July 5 - 14	1
July 14 - 21	2
Aug. 5 - 11	3
Aug. 11 - 22	4
Aug. 22 - Sept. 5	5
Sept. 22 - Sept. 27	6
Sept. 27 - Oct. 2	6A
Oct. 2 - Oct. 7	7
Oct. 7 - Oct. 10	8
Oct. 14 - Nov. 2	9
Nov. 2 - Nov. 19	10
Nov. 19 - Dec. 2	11

TABLE 4(b)
SAMPLING PERIODS AT STATION 270
DURING 1975

<u>Date</u>	<u>Time Period</u>
Oct. 10 - 14	1
Oct. 14 - 19	2
Oct. 19 - 23	3
Oct. 23 - 26	4
Oct. 26 - 29	5
Oct. 29 - Nov. 2	6
Nov. 2 - 5	7
Nov. 5 - 12	8
Nov. 12 - 19	9
Nov. 19 - Dec. 2	10

TABLE 5(a)

ESTIMATED HYPOLIMNETIC OXYGEN DEMAND (HOD)

STATION	258	270	#4
Average O ₂ in Hypolimnion on 11/6/75	4.8 mg ⁻¹	4.2 mg ⁻¹	3.6 mg ⁻¹
Average O ₂ in Hypolimnion on 26/6/75	1.0 mg ⁻¹	1.0 mg ⁻¹	0.9 mg ⁻¹
Estimated Depth of Hypolimnion During 11/26/6	16m	5m	9m
HOD (gm m ⁻² day ⁻¹)	4.1	0.8	1.6

TABLE 5(b)

ESTIMATED HARBOUR OXYGEN DEMAND, 1972
FOR A MEAN DEPTH OF 13m

- (1) O₂ stocks in May = 3×10^6 kg
- (2) O₂ stocks in July = 1.5×10^6 kg
- (3) Decline in O₂ stocks = 1.5×10^6 kg
- (4) Length of Period = 84 days
- (5) Estimated Oxygen Demand = $0.84 \text{ gm m}^{-2}\text{day}^{-1}$

TABLE 6
ESTIMATED OXYGEN DEMANDING LOADINGS

SOURCE		OXYGEN DEMAND
1.	COOTES PARADIZE (Estimate BOD = 10 mg/l ⁻¹ ; average flow = 70 cfs)	1,700 kg day ⁻¹ (3,800 lb day ⁻¹)
2.	INDUSTRIAL SOURCES	
	(a) BOD ₅	14,000 kg day ⁻¹ (31,000 lb day ⁻¹)
	(b) Ammonia - 2,700 lb/day (Assume complete oxidation by reaction, $\text{NH}_3 + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + \text{H}^+$ i.e. 17 lb NH ₃ =O ₂ demand of 64 lb)	4,500 kg day ⁻¹ (10,000 lb day ⁻¹)
3.	MUNICIPAL WASTEWATER TREATMENT PLANTS (WWTP)	
	(a) Burlington, BOD ₅	410 kg day ⁻¹ (900 lb day ⁻¹)
	(b) Hamilton, BOD ₅	6,800 kg day ⁻¹ (15,100 lb day ⁻¹)
	(c) Hamilton Bypass	
	(i) Bypass 7.5 days (Assume 100 mgd, 150 mg/l ⁻¹ as BOD ₅ calculated to an annual basis)	1,400 kg day ⁻¹ (3,100 lb day ⁻¹)
	(ii) Partial Bypass 40 days (Assume 55 mgd, 150 mg/l ⁻¹ as BOD ₅ calculated to an annual basis)	1,600 kg day ⁻¹ (3,500 lb day ⁻¹)
4.	TOTAL (67,400 lb/day) (Distributed on surface area basis, the O ₂ demand is equivalent to rate of 1.4 gm m ⁻² day ⁻¹ .	30,600 kg day ⁻¹

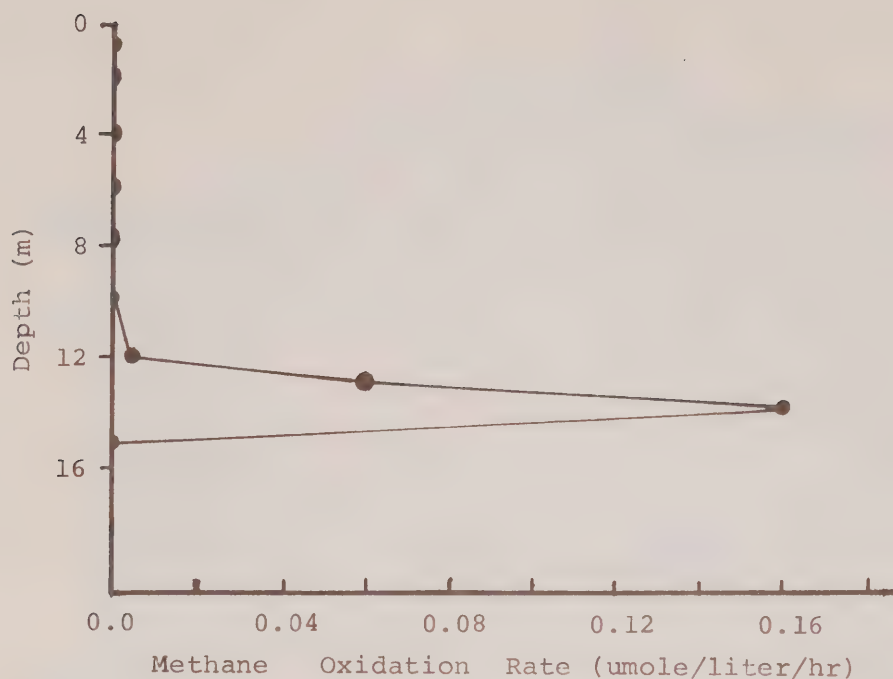


FIG. 1. TYPICAL PROFILE OF METHANE OXIDATION
(AFTER RUDD ET AL, 1974)

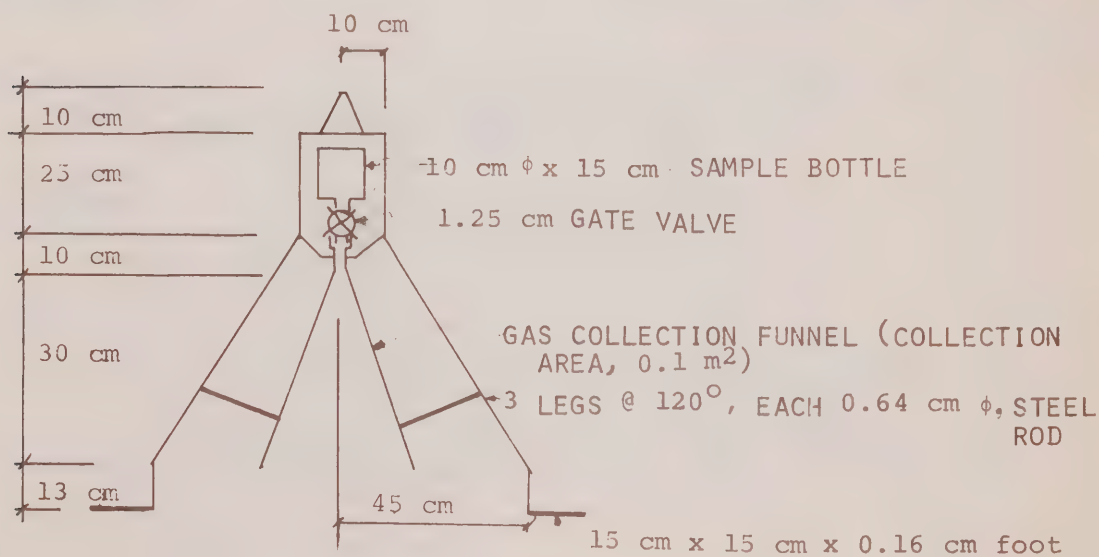


FIG. 2. GAS COLLECTOR (NOT DRAWN TO SCALE)

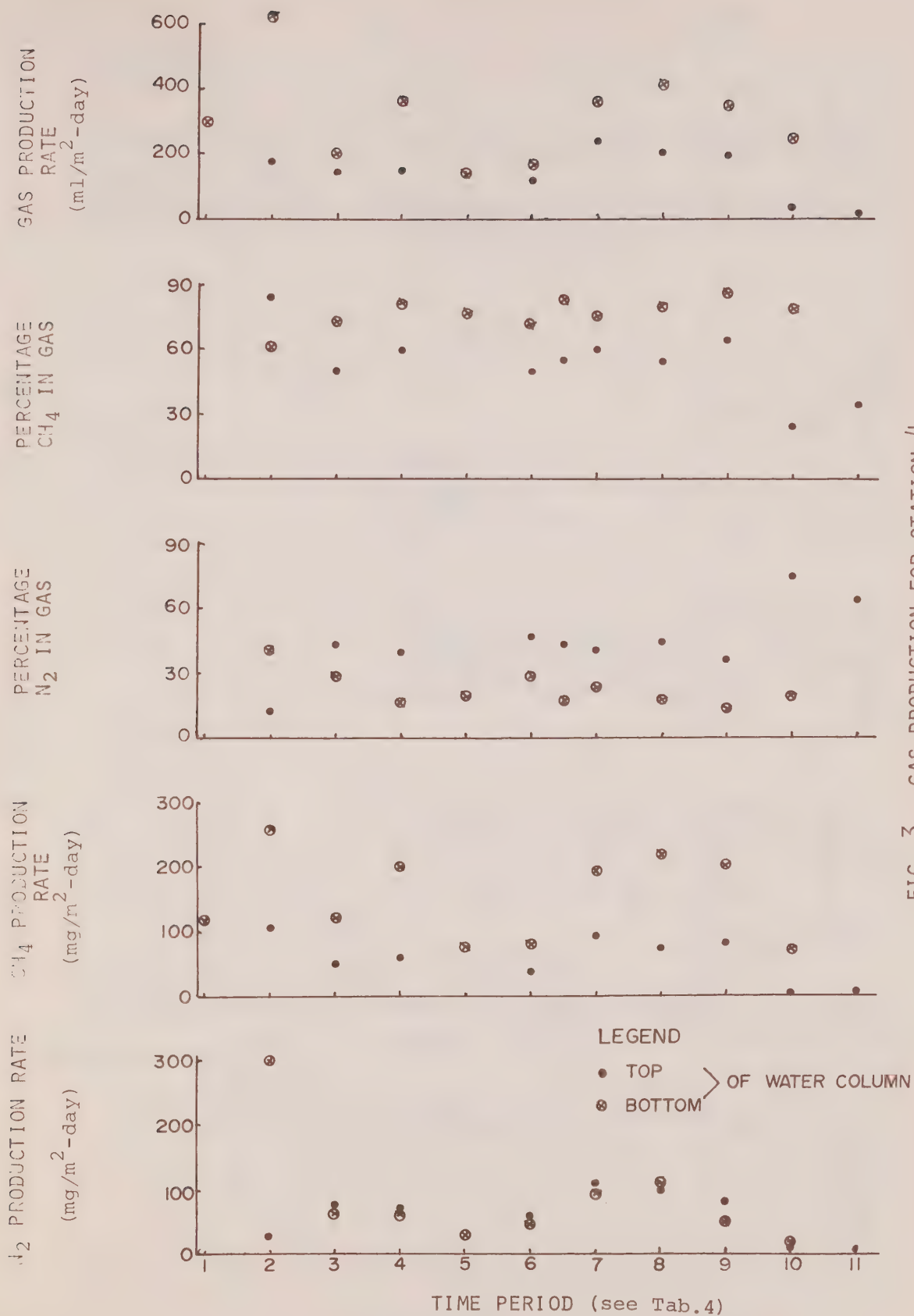
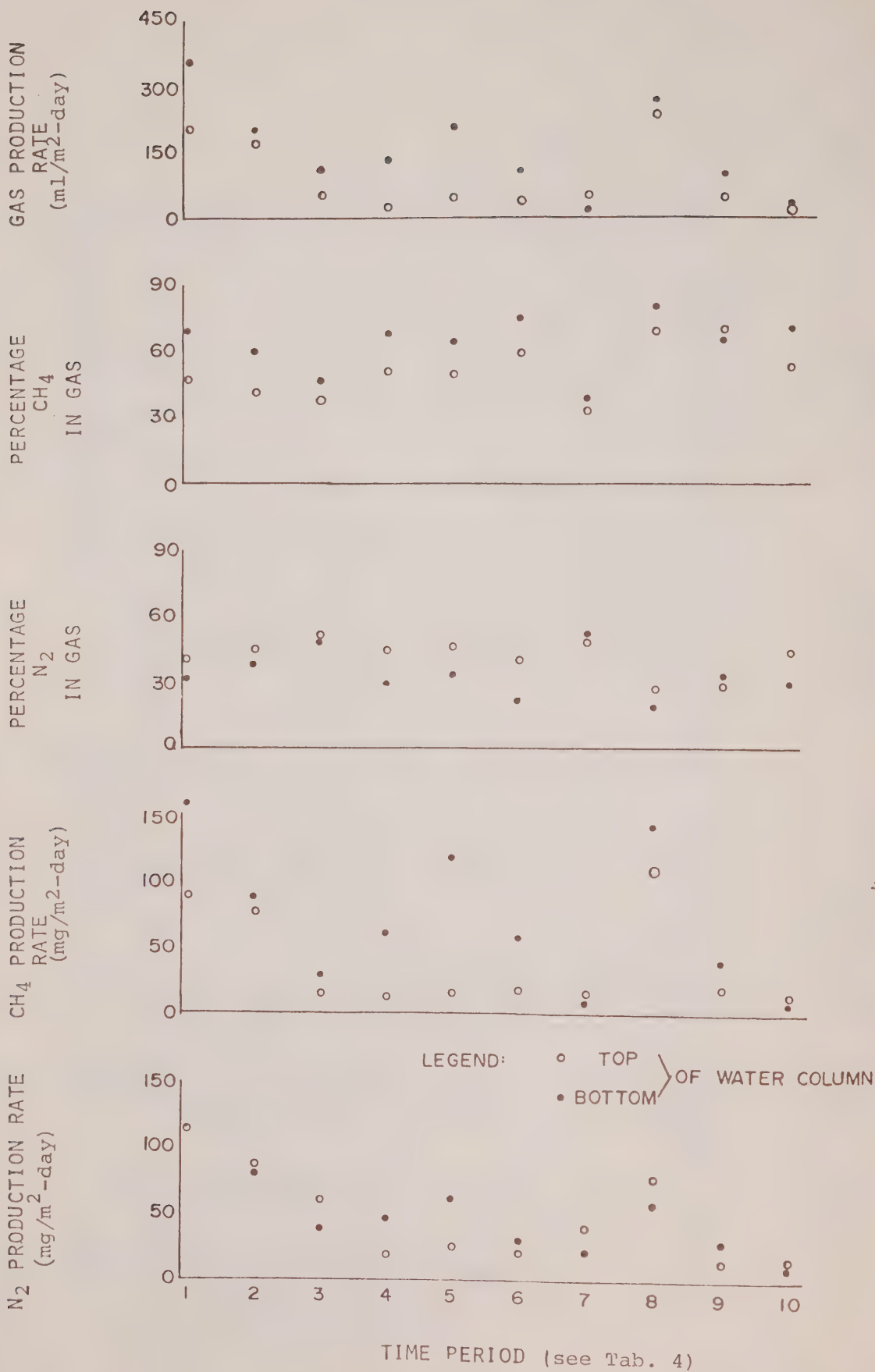


FIG. 3. GAS PRODUCTION FOR STATION 4



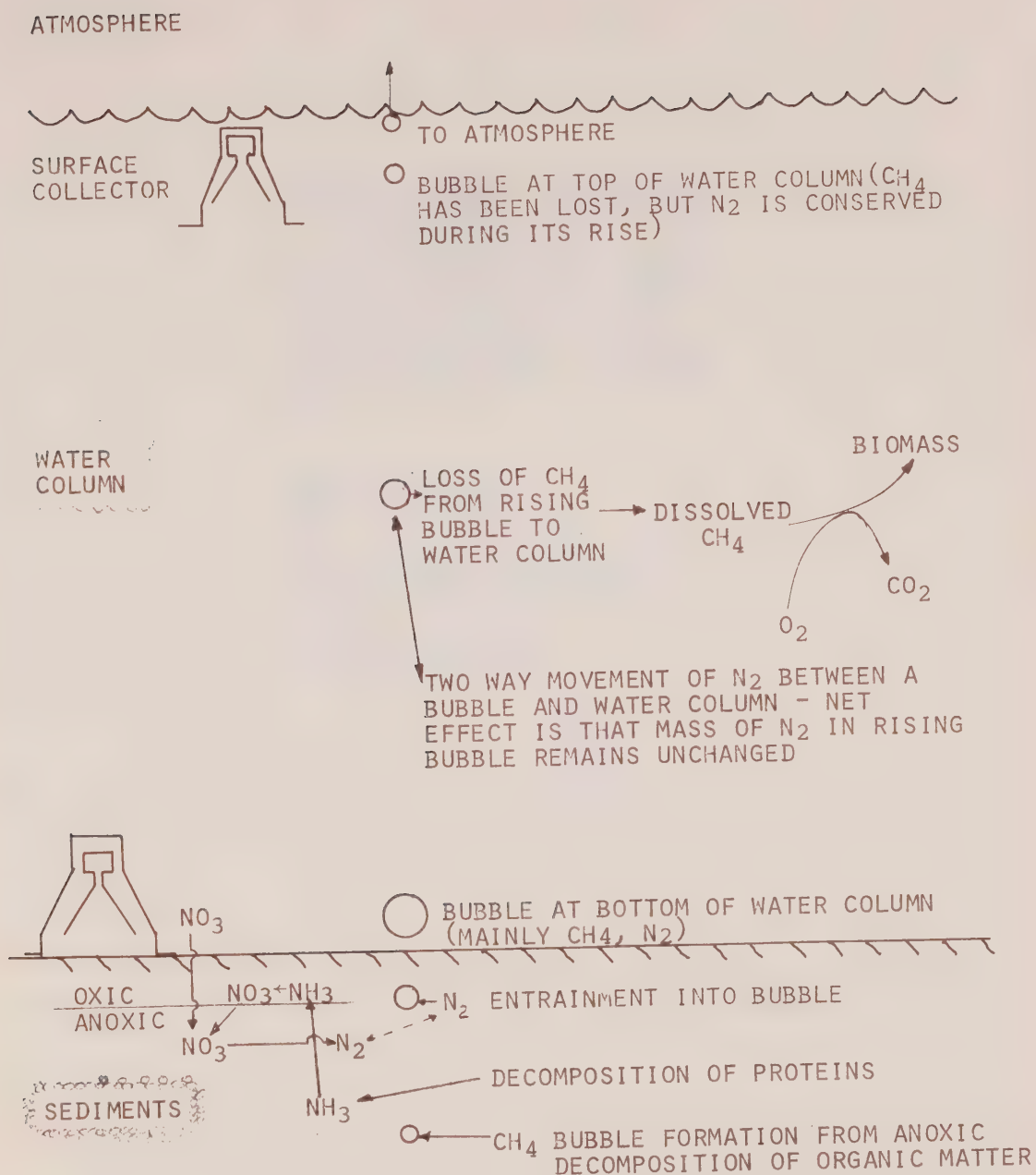


FIG. 5. CONCEPTUAL SKETCH OF MAIN PROCESSES AFFECTING GAS BUBBLE

HAMILTON HARBOUR STUDY '75

section E

Phytoplankton

–Bacteria

HAMILTON HARBOUR STUDY
SECTION E
BACTERIA AND PHYTOPLANKTON
SUMMARY

BACTERIA AND PHYTOPLANKTON WERE MONITORED AT FOUR STATIONS DURING 1975. PATHOGENIC INDICATOR SPECIES OF BACTERIA, PSEUDOMONAS <10/100 ML; TOTAL COLIFORMS <150/100 ML; AND FECAL COLIFORMS <100/100 ML, CONTINUED TO DECLINE AND FREQUENTLY MET WATER QUALITY STANDARDS. THIS DECREASE IN ABUNDANCE WAS POSSIBLY A DILUTION EFFECT OF VERTICAL MIXING. OCCASIONS OF HIGH BACTERIAL POPULATIONS WERE NOTED.

NITROSOMONAS, SULPHUR OXIDIZERS AND REDUCERS, AND GENERAL HETEROTROPHS COMBINED TO REPRESENT A LARGE PROPORTION OF THE BIOLOGICAL PRODUCTION OF THE HARBOUR.

PHYTOPLANKTON WERE NOT NUTRIENT LIMITED EXCLUDING A POSSIBLE SILICA LIMITATION OF THE SPRING DIATOM GROWTH. STANDING CROPS WERE MODERATE, AND WERE LIMITED BY LIGHT PENETRATION AND MIXING DEPTHS. PRIMARY PRODUCTION IS LOW, 1.0-1.5 GRAMS CARBON/M²/DAY, CONSIDERING THE EUTROPHIC NATURE OF THE HARBOUR WATERS. CHLOROPHYLL A WAS CONSIDERED TO BE A POOR ESTIMATE OF BIOMASS IN COASTAL WATERS.

INTRODUCTION

Eutrophication is often represented by an increase in biomass. Because of the association of trophic status and biomass, there is a tendency to define trophic states with chlorophyll a. This approach is of limited value as chlorophyll a depicts an unique portion of the total biomass and frequently underestimates biomass in some circumstances. In a highly eutrophic body of water, such as Hamilton Harbour, trophic status is poorly represented by chlorophyll a as a large portion of the biomass is bacterial in nature. When trying to assess the eutrophic status of lake systems, it is best to consider changes in the production and assimilation potentials as a result of enrichment. These potentials can be estimated by models of the energy flows within the system.

In Hamilton Harbour, maximum chlorophyll a concentrations have varied dramatically since 1972. This does not imply that trophic status has varied, but does suggest that in some way, phytoplankton production has been altered or cropping factors changed. Modifications of this production can be considered in regard to changes in the energetics of the system. As nutrients are abundant, these changes are probably related to the physical environment and/or toxicity.

The assimilation potential (the ability to stabilize loadings) of the harbour is strongly related to total biological production. Hypolimnetic anoxia is dependent on oxygen demanding transformations in the sediments which are mediated by the resident biological communities. Large oxygen demands are resultant of the respiration of large amounts of organic material. Once the oxygen has been depleted (see Foree and McCarty, 1970), the respiration of this organic material possibly becomes less efficient and the carbon material can accumulate in the sediments. Because of anoxia, the assimilatory potential (i.e. carbon flux) of Hamilton Harbour would decrease.

The organics which supply the carbon skeletons and energy for bacterial production are supplied by municipal and industrial wastes. Phytoplankton growths contribute a large amount of carbon to the sediments of Hamilton Harbour. This was confirmed by visual analysis of the sediments and the findings of remnants of diatoms and green algae and large loss on ignition data (up to 18 percent). In this regard, eutrophication is not simply represented by algal standing crops.

In the following sub-sections, the eutrophic state of Hamilton Harbour will be discussed with reference to the energy flows within and between the communities involved in determining the production and assimilation potentials of the harbour. The bacterial and phytoplankton dynamics are presented in separate sub-sections. A third sub-section will discuss responses of benthic organisms and fish.

BACTERIAL POPULATIONS

Excluding pathogenic indicator species of microbial populations are often ignored in water quality studies despite the major role they play in oxygen demand and nutrient cycles. Carbon cycling, such as the stabilization of dissolved organic matter and the production of carbon dioxide or methane, and sulfur and nitrogen cycles are dependent on the composition, abundance and activity of the naturally occurring bacteria. Little is known of the nutrient requirement of bacteria (Jones, 1971), but as mentioned by Overbeck (1974), it is becoming apparent that bacteria have significant influences on the production ecology of lakes. This is particularly true in Hamilton Harbour, where a large amount of the biomass is bacterial in nature. The abundance of eight taxons, as determined by plating techniques, would indicate that bacterial standing crops of the order of $10^5 \text{um}^3 \text{ ml}^{-1}$ are frequently achieved. This large bacterial standing crop approximates total phytoplankton volumes, thus the use of chlorophyll a as an indicator of biomass is indeed a tenuous procedure.

Bacteria samples were collected in Hamilton Harbour from April 22 to October 1975. Four stations (252, 270, 258 and 4) (see Fig. 1) were sampled at the surface and 1 m from the bottom of the harbour. Duplicate sterile bulbs were used for sampling, and the samples were taken to the laboratory on the day of collection. Taxa monitored included fecal coliforms, total coliforms, fecal enterococci, Nitrosomonas, Pseudomonas, heterotrophs, sulphur oxidizers and reducers.

Enterococci and Pseudomonas aeruginosa were found in very low numbers, but present in all samples. The abundance of Pseudomonas and enterococci was generally low in the open water stations (<10/100 ml) but with higher surface populations at Station 4 (>20/100 ml) (see Table 1). Figure 2 illustrates the temporal distribution of fecal coliforms, total coliforms and Nitrosomonas at four stations. Station 4 tended to have the highest surface populations as compared to other harbour stations, this being a function of its proximity to the Hamilton sewage treatment plant.

Table I presents the geometrical mean of the bacterial populations at the four stations monitored. Excluding station 252, concentrations are larger in the epilimnetic waters. The shallow depth of station 252 is not a sufficient explanation of increased bottom populations at this site. Mixing in a shallow water column should result in a more homogenous distribution and not a concentration effect near the bottom.

As noted in a previous section on artificial mixing, concentrations of fecal coliforms and enterococci were higher in the epilimnion than in the hypolimnetic waters. This is to be expected as the warm sewage effluent would tend to stay above the thermocline. There is no other major source for these bacteria, and as they do not grow in natural systems those found in the hypolimnion have apparently sedimented through the thermocline.

With respect to the assimilation capacity of the harbour, the most important group of bacteria were the heterotrophs. Heterotrophs are a diverse group including genera such as Achromobacter, Flavobacterium, Micrococcus and Pseudomonas. Dissolved organic substances from drainage, municipal wastes, and those produced by the phytoplankton are important carbon sources for the heterotrophs. As Hamilton Harbour has such a large resident population of this type of bacteria (Figure 3), nutrient availability and oxygen demand are probably frequently related to the heterotrophs and their production ecology.

There are no indications of the bacterial populations being nutrient limited as nutrient and bacteria fluctuations had little in common. Autochthonous bacteria in the harbour are probably using humic acids and other high molecular weight dissolved organic substances. On June 4, there was a decrease of filtered reactive phosphate coincident with a large bacterial growth. This growth occurred during incipient stratification of the harbour, and might well have been related to changes in the physical-chemical environment.

Using Strathmann's (1967) estimate for organic carbon content of phytoplankton

$$\log C \text{ (pg)} = 0.610 + 0.892 \log (\text{vol. um}^3)$$

it was estimated that 0.92 mg l^{-1} of carbon was associated with phytoplankton populations. If a similar amount is assumed to represent the bacterial populations as cell constituents are similar, less than $2 \text{ mg of carbon l}^{-1}$ can be accounted for by in situ production. As total organic carbon of the harbour is frequently in the range of 7 to 8 mg l^{-1} , there is up to 75 percent of the total organic

carbon which is allochthonous in nature, probably from municipal and industrial wastes. With respect to water quality, such as oxygen content and water colour, organic loadings are probably as deleterious as phosphate loadings into the harbour. There was no statistical relationship between carbon and chlorophyll a ($R=0.17$) or TOC and BOD ($R=0.24$). Variations in the organic content of the harbour are not strictly dependent on fluctuations in the algal or bacterial populations.

Total coliforms, and some enterococci determinations (see Table 1) suggest that the surface waters of Hamilton Harbour were not suitable for body contact recreation generally. Station 4 had the highest population with a geometric mean of fecal coliforms of 205 counts 100 ml⁻¹ yet the open water stations 258 and 270 had geometric means of 62 counts 100 ml⁻¹ and 41 counts 100 ml⁻¹ respectively. It must be noted, however, that geometric means do not include samples in which populations were too numerous to determine an accurate count, and sampling did not meet the criteria of 10 samples per station per month.

TABLE 1: Bacterial Populations of Hamilton Harbour, 1975
(Geometric Means 100 ml⁻¹, Apr 22-Aug 19; 17 samples)

Taxa	Stn 4	Surface		Stn 270
		Stn 252	Stn 258	
Total Coliform	5,066	1,254	2,125	827
Fecal Coliform	205	70	62	41
Enterococci	11	3	2	3
Pseudomonas	27	4	3	2
Heterotrophs	160,000	80,000	69,244	31,000
Nitrosomonas	1,190	325	364	341
Sulphate Reducers	253	75	37	26
Theoparus	9,960	8,551	8,864	5,184

Taxa	Stn 4	Bottom		Stn 270
		Stn 252	Stn 258	
Total Coliform	1,460	2,588	313	566
Fecal Coliform	73	135	19	51
Enterococci	3	21	1	4
Pseudomonas	5	5	2	1
Heterotrophs	63,272	108,321	40,930	39,164
Nitrosomonas	783	751	410	409
Sulphate reducers	58	158	20	32
Thioparus	1,091	8,481	1,751	1,550

There were no simple trends in the distribution and abundance of Nitrosomonas, sulphur reducers or sulphur oxidizers (see Figure 3). The latter taxa indicated that the assimilation

potential changed during artificial mixing as sulphur reducers decreased in abundance and sulphur oxidizers increased. As the presence of sulphide is toxic to methane producing bacteria, a maintenance of low sulphide production might result in increased methane production. The natural consequences of such a response could result in a more rapid stabilization of the organic contents of the sediments of Hamilton Harbour (Foree and McCarty, 1970). It is debatable that the maintenance of an oxidized microzone would result in greater rates of carbon stabilization than would occur under anaerobic conditions. There is, however, the aspect that aerobic conditions would result in products from the stabilization process which are not deleterious to the general water quality of the harbour. It is therefore desired that the stabilization of the sediments of the harbour be achieved by aerobic processes. The major difference of aerobic decomposition would be the prevention of sulphide toxicity effects, and that products of aerobic respiration such as CO_2 do not create an oxygen demand in the water column.

Heterotrophic bacteria (Figure 3) appeared to be distributed similarly to the fecal coliform organisms with higher populations at stations 4 and 252. The majority of the heterotrophs are suspected to be of autochthonous origin, thus the association of heterotrophs and coliform organisms is peculiar. The distribution might reflect the response of the heterotrophs to areas of increased organic loadings.

The bacterial aspects of the water quality of Hamilton Harbour are not conducive to contact recreation. Although artificial mixing apparently reduced populations, it is not wise to generalize that contact recreation would result from continued mixing. Further refinements of sewage treatment are still essential to manage population abundance of the organisms. As noted in the previous report (MOE, 1975) concerning the water quality update, there continues to be a trend of improvement in the bacteriological water quality. This trend is tenuous considering the sparse sampling routine of the preceeding years.

In retrospect, after one year of intensive survey, the bacteria have been found to represent a large proportion of the biological production of the harbour. Water quality has not changed significantly with respect to coliform indicator organisms, but the initial effects of artificial mixing were promising. From the study it is strongly recommended that estimates of biological production as related to eutrophication include bacterial populations. High standing crops combined with short regeneration times would suggest a large proportion of the production of Hamilton Harbour is bacterial.

PHYTOPLANKTON

Modifications in the physical-chemical environment of the aquatic habitat result in pronounced changes in the size, composition and periodicity of phytoplankton standing crops. No single parameter dictates all possible responses. This is evident in the literature with particular regard to nutrients, photosynthetic available radiation and mixing depth. Nutrients are frequently associated as being factors which can limit phytoplankton standing crops, but do not affect the photosynthetic production rate per unit chlorophyll a. The latter is more related to the light climate of the lake (Talling, 1966; Megard, 1972), which is strongly influenced by mixing depth. Secondary responses by the phytoplankton population are related to cropping factors which might limit standing crop. Cropping might be in the form of grazing, dilution or sedimentation, and these pressures are independent of the growth potential of the phytoplankton.

Artificial mixing has been reported to alter nutrient availability and utilization by phytoplankton. Lorenzen and Mitchell (1975) noted that phytoplankton did not make use of available nutrients in Kesteven Lake during a period of artificial destratification. Reports such as this, and others (Ridley, 1972, Steel, 1972, Lund, 1965) would suggest that phytoplankton production and standing crops are not simple functions of nutrient loading. The validity of two-dimensional representation and correlation of algal standing crops and any other physical or chemical parameter is dependent on many other factors remaining constant.

Hamilton Harbour, because of its geometry, morphology and shoreline development, has a mosaic of environments to which the phytoplankton respond. Generalizations of phytoplankton production are questionable in such circumstances, unless surveys are designed to determine the temporal and spatial distribution patterns of standing crops.

Four stations were sampled during 1975 as described in the previous subsection. A combined study by the Ontario Ministry of the Environment and McMaster University in association with Professor G. P. Harris was initiated April 1975. Phytoplankton samples were collected at three depths representative of the top, middle and bottom of the water column at each station. Chlorophyll a was collected at 0.2, 3.0, 6.0, 12 and 18 meters to estimate the vertical structure of the phytoplankton populations. Samples were enumerated, after sedimentation, using the Utermohl technique (1931).

Counting procedures were as outlined by Lund, Kipling and LeCren (1958). McMaster University performed studies on primary productivity, nutrient availability and zooplankton abundance. Results are published independently in a separate report (Harris, 1976). MOE personnel collected algal samples for independent enumeration along with data on nutrients, metals and light penetration.

Physical-chemical parameters were determined weekly for each sample. Turbidity, filtered reactive phosphorus, nitrate, ammonia, total organic carbon and vertical attenuation of solar radiation were measured. The composition of the phytoplankton was similar to that outlined in a previous harbour report (MOE, 1975). Green algae dominated the plankton during the late spring and summer months. In the vernal and autumn periods of high natural turbulence diatoms were more abundant. Blue-green populations never developed to any significant size and many of the more ubiquitous species were only viewed infrequently.

A majority of the more common species of green algae were members of the Chlorococcales. Genera such as Oocystis, Coelastrum, Lagerheimia, Selenastrum, Kirchneriella, and Ankistrodesmus were abundant in the harbour waters, and were frequently observed at all times of the year. Other taxa of the Chlorococcales were genera such as Dictyosphaerium, Pediastrum, and Actinastrum which did not contribute much to the total phytoplankton biomass (less than 10%).

Another order of the green algae, the Volvocales, was well represented by a variety of species of Chlamydomonas and Pandorina morum (Muell) Bory. Palmelloid forms, including Gleocystis and Sphaerocystis, were frequently observed but did not achieve populations of any significant abundance.

The most important species of the summer phytoplankton were Oocystis borgei Snow., Pandorina morum Bory. and Cryptomonas spp. Oocystis dominated the plankton from late June throughout the summer, excluding a large, temporary pulse in late July, of Ankistrodesmus falcatus (Corda) Ralfs. ($4.3 \times 10^7 \text{ um}^3 \text{ ml}^{-1}$) (see Figure 4). This is similar to observations in 1974 when Oocystis dominated the plankton, but a large growth of Ankistrodesmus was not observed that year. In 1975, populations of Oocystis reached a peak of $5.2 \times 10^6 \text{ um}^3 \text{ ml}^{-1}$ in the surface waters. As would be suggested in the chlorophyll profiles (Figure 5) all growths of Oocystis were limited to the upper 5 m of the water column.

There was no indication of nutrient limitations within the harbour. Bioassay studies (Professor G. Harris, McMaster University) indicated that growths were basically light

limited, and inoculation of phosphorus, nitrogen or trace elements did not stimulate growth. There was, however, some evidence of zinc toxicity revealed by bioassay experimentation.

Cryptomonas spp. were abundant at most times of the year at all stations sampled. Cryptomonas erosa Ehrenb. and C. curvata Ehrenb. and C. rostratiformis Skuja and possibly Cryptomonas ovata Ehrenb. were the dominant species in the taxonomically complex group. Rhodomonas minuta Skuja had two growth pulses related to periods of vertical mixing, but because of its small size did not contribute significantly to the algal biomass of the harbour.

Blue-green algae were scarce with only Oscillatoria limnetica and O. planktonica being frequently observed. Genera such as Aphanizomenon, Anabaena and Microcystis which are usually common in eutrophic waters were absent from most samples. The presence of the green algae would suggest that nutritional requirements including carbon dioxide, iron and micronutrients were available, and it is probable that physical factors were limiting the production of the blue-green populations.

On most occasions, Hamilton Harbour could be considered to be a nutrient saturated environment. There were no observations of nitrogen limitation as $\text{NO}_3^- \text{N}$ ranged from 0.48-4.0 mg l^{-1} , and $\text{NH}_3^- \text{N}$ ranged from 0.01-4.1 mg l^{-1} . It was not determined which of the nitrogen forms were preferred for algal production as standing crops were similar no matter which nitrogen species dominated. Ammonia was more abundant in the spring, and it would appear as if the vernal diatom growth could efficiently utilize this nitrogen source. Variations in nitrate were not related to changes in chlorophyll a over the year, but summer populations showed some coherence (Figure 6).

Silica stores declined during the spring diatom growth from an average of 1.3 mg l^{-1} in late April to 0.87 mg l^{-1} in early June. Much of the silica was utilized by Stephandiscus hantzschii Grun.

A short pulse of another diatom, Synedra ulna (Nitzsch Ehr., further depleted silica concentrations during June, and by the first week of July silica values were averaging 0.29 mg l^{-1} . These low values predominated during the summer months as a result of continued silica uptake by an unidentified species of Cyclotella which became moderately abundant in August. A second growth of S. hantzschii was initiated in October, but did not achieve significantly large populations. This might have been the only occasion in which nutrients limited algal production within the harbour.

Alkalinity (85-112 mg l^{-1}) and pH (7.2-8.3) indicated sufficient carbon stores to support large algal populations. Conductivity (440-600) values suggested high salt dissociations and that nutrients were readily available to the biological system.

There were no obvious relationships of filtered reactive phosphorus and phytoplankton standing crops. This is not unusual in eutrophic environments such as Hamilton Harbour where there is more phosphorus than is required to support the maximum crops achieved within that body of water. Fluctuations in the filtered reactive phosphorus are not correlated with the chlorophyll a concentration (see Figure 6), and it is not known what is the source of the temporal variations found within the soluble phosphorus data.

At no station was there a high correlation between chlorophyll a and total phosphorus. The best relationship was at Station 258 where chlorophyll a and total phosphorus were related by the following relation:

$$C'_{\text{phyll a}} (\text{mg m}^{-2}) = 0.17 (\text{TP}) + 0.01 \quad r=0.62$$

which was significant at the 5 percent level. The remaining stations, however, had much poorer fits as outlined below:

Stn 4	$C'_{\text{phyll a}} (\text{mg m}^{-2})$	$= 0.14 (\text{TP}) + 0.07$	$r = 0.45$
Stn 252	$C'_{\text{phyll a}} (\text{mg m}^{-2})$	$= 0.11 (\text{TP}) + 0.13$	$r = 0.30$
Stn 270	$C'_{\text{phyll a}} (\text{mg m}^{-2})$	$= 0.21 (\text{TP}) + 0.13$	$r = 0.42$

suggesting total phosphorus and chlorophyll a were not significantly related within the harbour environment.

The combined effects of the euphotic and mixing depths can influence the prediction of standing crop from a single parameter such as total phosphorus. This is supported by the work of Lorenzen and Mitchell (1975), which illustrated that physical factors influenced nutrient utilization. When applying models to predict standing crops it would be wise to confirm that the product (ϵZ) of the vertical attenuation coefficient (ϵ) and the mixing depth (Z_m) does not greatly exceed 4.6 (see page 12). In most lakes, however, as eutrophication increases these values of ϵZ tend to exceed 4.6 because of self-shading and remnant particles from previous growths of algae. Extrapolation of relationships developed from data on oligotrophic lakes should be viewed with caution. Thermal instabilities and varying light penetrations such as those evident in Hamilton Harbour increase the variability in the nutrient-standing crop relationships. Light penetration in the harbour was not related to turbidity which was frequently measured below 4 FTU.

An unique aspect of Hamilton Harbour is that the water column does not thermally stabilize for extended periods of time. This results in an inter-active effect of light penetration and mixing depth and influences algal production

by modifying production rates and nutrient utilization. Vertical light attenuation in Hamilton Harbour is relatively high. Vertical attenuation coefficients range from 0.52-1.58 limiting the euphotic depth to 8.8-3.0 m respectively.

A self-shading coefficient for a composition of the most dominant species of Hamilton Harbour was determined by a regression analysis of chlorophyll *a* and the vertical attenuation coefficient. A value of 0.012 in units m^{-1} per unit chlorophyll *a* ($R=0.77$) was selected as the self-shading coefficient (ϵ_s) and is in agreement with the general range of values found of 0.008-0.022. The rather low amount of variability of the vertical attenuation coefficient accounted for by chlorophyll *a* was reasonable, considering the number of external factors such as changes in water colour, per cell chlorophyll content and phytoplankton composition which altered the relationship.

The self-shading coefficient (ϵ_s) accounted for vertical attenuation of solar radiation in the harbour waters in the range of 0.18-0.82, with a general background attenuation (water colour and non-productive material) averaging 0.62. Without any photosynthetically productive particles, Hamilton Harbour would have had an euphotic depth of approximately 15 m at the time of the maximum crop observed in 1975 as the attenuation coefficient resultant from non-algal material was determined to be 0.31.

Hamilton Harbour is an optically deep body of water (euphotic depth is less than mixed depth). The photosynthetic integral presented by MOE (1975) suggested that photosynthetic profile is contained within the water column when the extinction depth (ϵZ_m) is greater than 4.6. Values of the extinction depth (ϵZ_m) in the harbour during 1975 ranged from 6.2-19.0, and frequently more than 80 percent of the phytoplankton production was contained within the upper 2 m of the water column.

Column photosynthesis was determined using the above-mentioned integral. Relevant data and gross column photosynthetic production ($\text{gms carbon m}^{-2} \text{ hr}^{-1}$) are presented in Table II.

TABLE II: Primary Production Hamilton Harbour (Natural Populations)

Date	$\text{gC/mgC'phyll/m}^3/\text{hr}$	I_0^*	I_k	n	$\text{T}\bar{\text{T}}$	Theoretical $n_f\text{Pzdz}$ $\text{O}^{-2} \text{ hr}^{-1}$ gCm^{-2}	Experimental $\text{gCm}^{-2} \text{ hr}^{-1}$
Jul 14, 1975	0.003	1230	120	53	2.1	0.11	0.13
Jul 21, 1975	0.002	1235	130	49	1.6	0.08	0.12
Jul 28, 1975	0.001	1230	118	47	1.8	0.04	0.07
Aug 5, 1975	0.001	1213	130	41	1.3	0.06	0.06
Aug 11, 1975	0.001	1220	190	54	1.4	0.05	0.09
Aug 18, 1975	0.001	1263	80	52	1.5	0.08	0.10
Aug 25, 1975	0.001	1233	100	67	1.8	0.03	0.08
Sep 2, 1975	0.001	1247	70	23	1.6	0.05	0.05
Sep 9, 1975	0.002	235	130	32	1.5	0.05	0.01
Sep 15, 1975	0.002	232	100	21	1.1	0.05	0.09
Sep 23, 1975	0.002	240	170	18	0.7	0.06	0.08
Oct 14, 1975	0.002	1254	70	19	1.1	0.02	0.05

List of Symbols:

- $\text{P}_{\text{max.}}$: Maximum observed rate of photosynthesis per unit chlorophyll a.
 I_0 : Average surface light intensity during study.
 I_k : Light saturation value of natural population.
 n : Chlorophyll a concentration in mixed layer.
 $\text{T}\bar{\text{T}}$: Vertical attenuation coefficient of photosynthetic available radiation.

Maximum production occurred during July and gradually decreased until the middle of August. This decrease continued into the autumn, possibly as a result of declining light and a switch to phytoplankton species capable of heterotrophic carbon assimilation.

Although the highest standing crops expressed as chlorophyll a or number of cells per unit volume occurred in the summer, maximum standing crops (chlorophyll a mg m^{-2}) occurred in the spring when diatoms dominated the phytoplankton. Figure 7 outlines the standing crop measured as chlorophyll a mg m^{-2} at the four primary stations. Station 4 produced the highest summer crops (563 mg m^{-2} chlorophyll a). It is interesting to note that the shallow epilimnetic station (no. 252) produced higher summer standing crops (330 mg m^{-2} chlorophyll a) than the deeper station 270 (219 mg m^{-2} chlorophyll a) and approached the production of the deepest station 258 (334 mg m^{-2} chlorophyll a).

If there was no background attenuation of solar radiation, maximum standing crops could be achieved when the mixing depth Z_m equalled the euphotic depth Z_{eu} . This can be theoretically supported as the vertical attenuation coefficient (ϵ_t) of solar radiation is an additive function.

$$\epsilon_t = \epsilon_q + \epsilon_p \quad (1)$$

Where ϵ_p is the attenuation resultant from productive particles, and ϵ_q is the attenuation resultant from non-productive particles, water colour and natural absorption of the longer wave lengths of light by water.

The euphotic depth (1% of surface light intensity) is often coincident with a mixing depth during summer stratification, but as the summer progresses the ratio $Z_{eu}:Z_m$ decreases, and this can reduce standing crop by limiting production. Sverdrup (1947) had noted that production decreased logarithmically with mixing depth, unless there is an uneven vertical distribution of organisms.

Because of the definition of the euphotic depth it can be shown that:

$$0.01 = e^{-\epsilon_t Z_{eu}}$$

and therefore

$$Z_{eu} \epsilon_t = 4.6$$

It might be noted, however, that Talling (1965) proposed a correction for spectral modification such that:

$$Z_{eu} \alpha \epsilon_t = 3.7 \quad \text{where } \alpha = 1.33$$

This correction resulted in a closer correlation of measured and predicted production as illustrated in Table II. For the purpose of resolving the effects of light and mixing on algal production the uncorrected value of 4.6 is adhered to.

ϵ_p is a product of the cell shading coefficient (ϵ_s) and biomass (N). The background attenuation coefficient (ϵ_q) is difficult to measure directly, and some investigators assume ϵ_q is constant in all bodies of water, or approximates 0. Under these assumptions, prediction of maximum biomass is elementary.

$$\text{As } Z_{eu} \epsilon_t = Z_{eu} N \epsilon_s + Z_{eu} \epsilon_q$$

$$\text{and } Z_{eu} \epsilon_q = 0$$

then maximum biomass ($c'phyll \underline{a} \text{ ug } l^{-1}$)

$$N_{max} = \frac{4.6}{\epsilon_s Z_{eu}} \quad (\text{see Figure 7}) \quad (2)$$

Unfortunately, as seen by the variability of secchi disc-chlorophyll a relationships, ϵ_q can vary. In Hamilton Harbour it was found that ϵ_q varied dependently with ϵ_t . If it was assumed that $\epsilon_q = 0.44 \epsilon_t$ (as determined by linear regression ϵ_q and ϵ_t) than some variations in background attenuation can be accounted for as:

$$Z_{eu} \epsilon_t = Z_{eu} N \epsilon_s + Z_{eu} (0.44 \epsilon_t)$$

$$4.6 = Z_{eu} N \epsilon_s + 0.44 (4.6)$$

$$2.6 = \epsilon_s N Z_{eu}$$

$$N_{max} = \frac{2.6}{\epsilon_s Z_{eu}} \quad (\text{see Figure 7}) \quad (3)$$

which would be suitable for environments of constant mixing depth or which are thermally stabilized during the period of interest.

Riley (1942, 1943) observed that the rate of increase in a phytoplankton population was a linear function of the reciprocal thickness of the turbulent zone. This infers that

$$N_{max} = f \left(\frac{1}{Z_m} \right) ;$$

and Sverdrups observation would suggest the production and light penetration were directly related such that

$$N_{max} = f' (Z_{eu})$$

when

$$Z_m \epsilon_t = 4.6 \text{ then } \frac{Z_{eu}}{Z_m} = 1$$

In optically deep bodies of water $Z_m \epsilon_t > 4.6$, and therefore Z_{eu}/Z_m is less than one. Under these conditions, production and standing crop tend to become light limited and are modified according to the $\epsilon_t Z_m$ value for that particular water column. Thus equation (3) which assumes mixing depth = euphotic depth can be modified to correct for occasions when $Z_{eu} < Z_m$. A more general expression for Hamilton Harbour would be:

$$N_{\max} = \frac{2.6}{\epsilon_s Z_{eu}} f(i) \quad (4)$$

$$\text{where } f(i) = \frac{4.6}{Z_m \epsilon_t} \quad (5)$$

Values of $f(i)$ can vary according to the water column in particular, and one lake can have different values on the same occasion.

This expression permits an estimation of standing crop assuming a linear relationship exists between ϵ_q and ϵ_t . It is apparent (see also Kirk, 1975 a,b) that standing crop is maximized as ϵ_q approaches 0 and the cell shading coefficient (ϵ_s) is reduced. ϵ_s can be decreased by cells with large volume-area relationships (i.e. large spherical cells). There are indications, however, that no direct relationships of ϵ_s and cell diameter exist possibly because of forward scattering properties of small particles and the response of cell size to light attenuation would be more complex than a simple linear relation.

In Figure 8, two theoretical maxima of phytoplankton are illustrated as functions of the vertical attenuation coefficient. The first maximum assumed no background attenuation of photosynthetic available radiation, and is determined by substituting $4.6/\epsilon_t$ for Z_{eu} in equation 2. A second maximum assumed variable background attenuation dependent on the measured vertical attenuation coefficient. Measured chlorophyll *a* values frequently approached this second maximum, suggesting it was more realistic to predict crops within the harbour environment. Points which do not fit reflect a dominance of *Cryptomonas* spp in the plankton or the autumn sinking of the thermocline such that $Z_m \gg Z_{eu}$.

Phytoplankton standing crops and production in Hamilton Harbour are distinctly light limited. Because of the previously discussed relationships of light penetration and mixing depth, artificial mixing will strongly influence the composition and duration of algal growth within the harbour.

These calculations assumed chlorophyll a is a good estimate of phytoplankton standing crop. When comparing algal volume and chlorophyll a there are several interesting aspects which affect the interpretation of the data from the harbour. In Figure 9 it is illustrated that chlorophyll a content can be predicted within a 95% confidence interval from cell volume with a correlation of $r=0.65$. Despite the apparent statistical fit, it is notable that only 40% of the variation in chlorophyll a can be accounted for by volume. Chlorophyll a content per unit algal volume varied from 2.4×10^{-10} - 1.0×10^{-8} ug μm^{-3} . High values were obtained during the onset of artificial mixing suggesting an increase in cell chlorophyll to compensate for deeper vertical circulation of the cells. The chlorophyll a profiles at station 258 (Figure 5) suggested a piling up of the phytoplankton within the metalimnion, indicating restricted vertical mixing at that depth. This accumulation of cells was not apparent towards the end of July during the period of the most intensive mixing. A similar explanation of increased mixing depth might account for the September increase in per unit algal volume chlorophyll.

The effect of algal composition on log chlorophyll a - log volume relationships was well illustrated in October when there was no correlation ($R=0.10$), between algal volume and chlorophyll. Various species of Cryptomonas such as C. ovata, C. rostratiformis and C. erosa dominated the plankton, and were possibly obtaining a relatively large amount of carbon via heterotrophic assimilation. The decline in chlorophyll:algal volume on July 28, was possibly a result of the heterotrophic properties of Ankistrodesmus (Zajic and Chiu, 1969).

Although phytoplankton crops of the harbour are frequently light limited, many of the forms which dominate during periods of natural and artificial mixing such as Stephanodiscus, Ankistrodesmus or Cryptomonas are suspected of being able to obtain carbon from sources other than photosynthetic assimilation, and hence are well adapted to vertically unstable water columns where Z_m is greater than Z_{eu} . Although large variations in the standing crop occur, it is possible that these often reflect changes in ϵ_q or differences in the rates of heterotrophic assimilation and photoautotrophism.

Other variations in chlorophyll per unit algal volume might reflect the possibilities of toxicity. Bioassay work by McMaster University, suggest that one effect of zinc toxicity is the lowering of the chlorophyll per cell content. Should varying levels of zinc toxicity be occurring, estimates of ϵ_s would be affected.

Phytoplankton production ecology of the harbour is complex, and cannot be accurately simplified into a two-dimensional correlation. Sophisticated models, such as Lehrmann (1975) and Bannister (1974) cannot be applied until a more detailed study of the kinetics of production of the species involved is completed. Another aspect, not yet considered within any model of phytoplankton production, is that spectral modification can influence the production of optically deep bodies of water where a majority of photosynthetic carbon is assimilated in the upper two meters. Such modification should profoundly influence cell size and pigment content, and result in definite changes in the composition of the flora.

Hamilton Harbour frequently supports large algal growths ($>10^6 \text{ } \mu\text{m}^3 \text{ ml}^{-1}$), and there is little evidence of nutrient limitations. In many circumstances, phytoplankton appear to be light limited although marked variations do occur. Although seston heterogeneity might account for some of this variability, biotic responses or toxicity might play a major role. As in many other environments, simple correlations do not account for the variations observed.

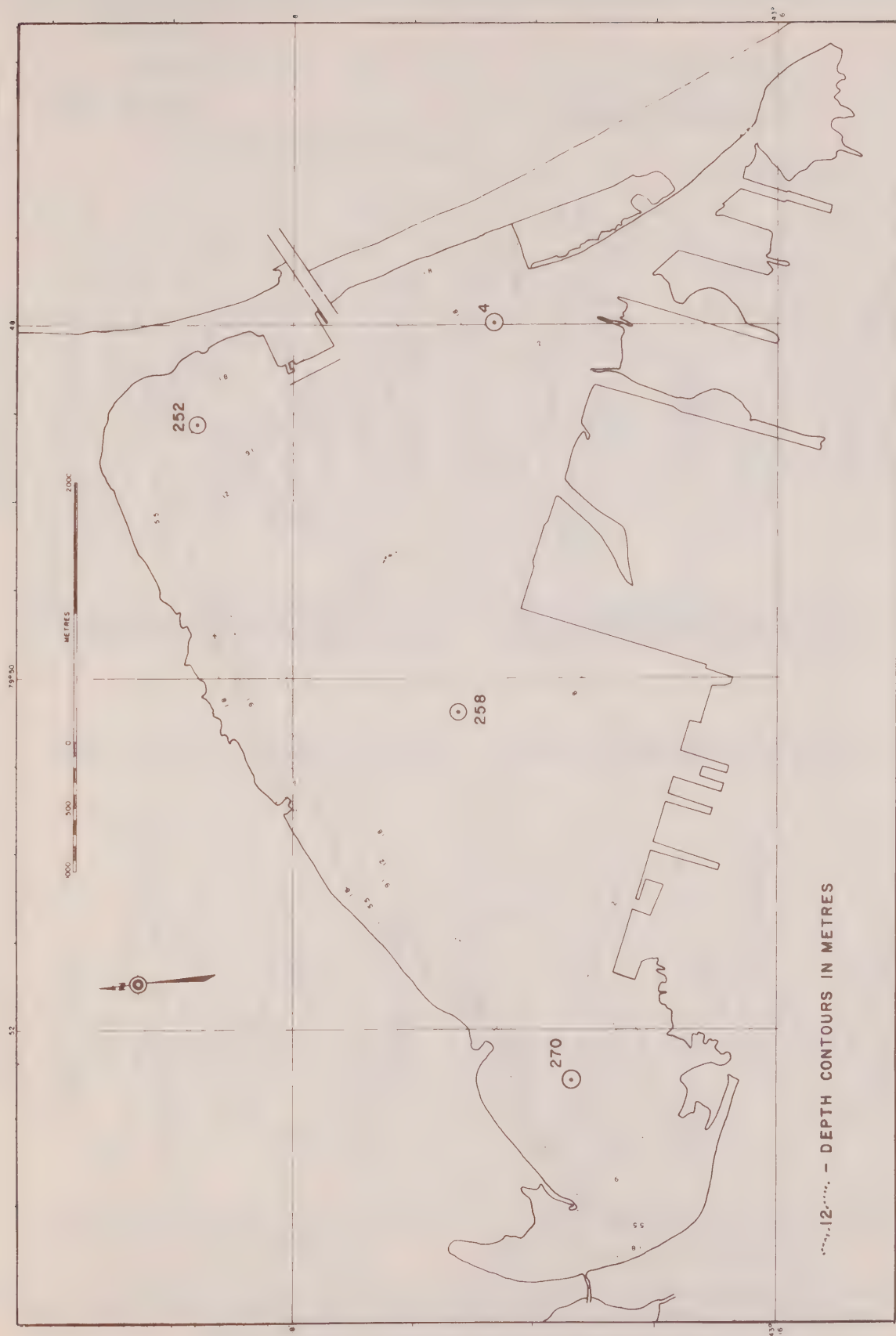
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.....12..... - DEPTH CONTOURS IN METRES

FIGURE 1 : HAMILTON HARBOUR AND FOUR PRIMARY SAMPLING STATIONS.

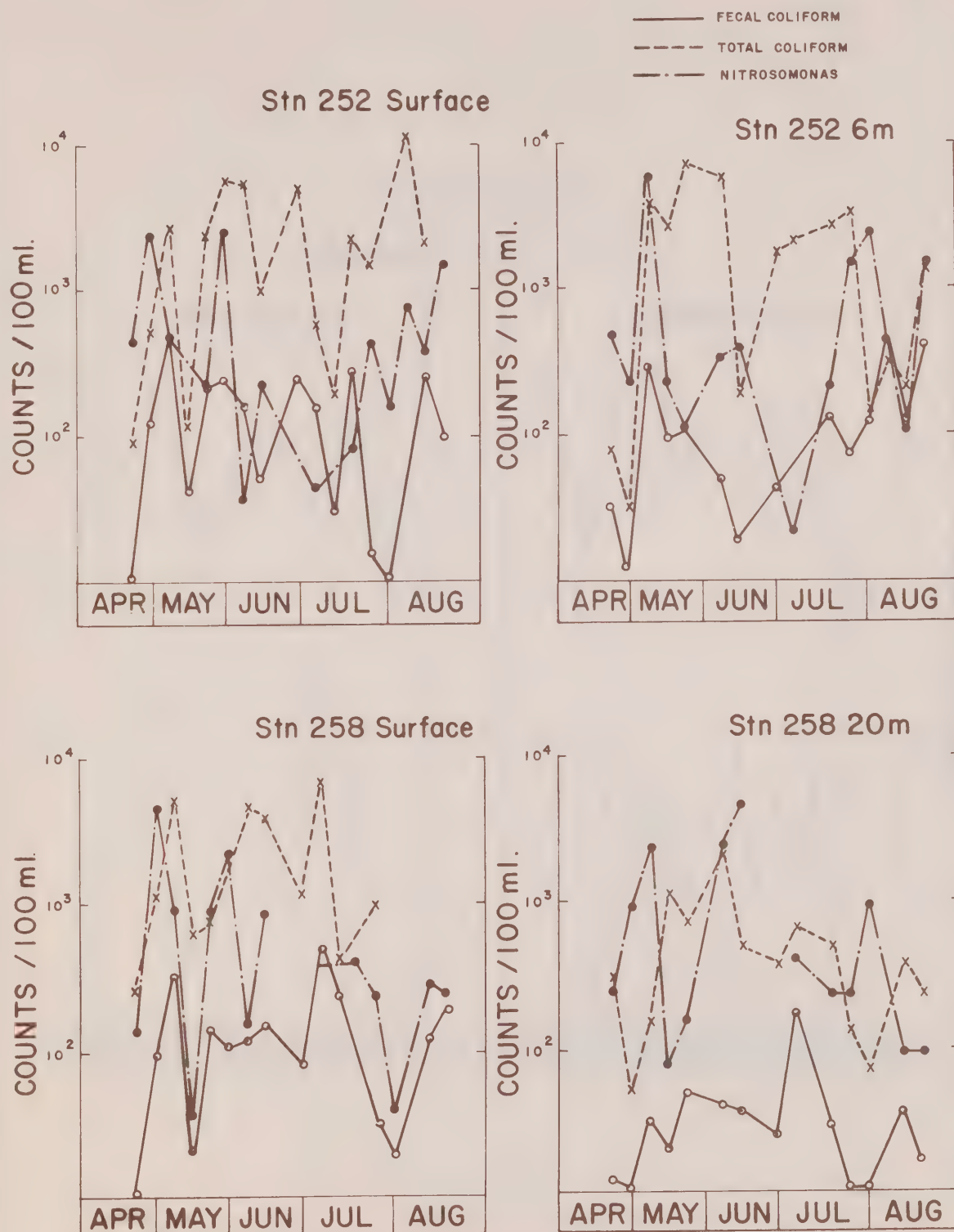


FIGURE 2b: TEMPORAL DISTRIBUTION OF COLIFORM BACTERIA AND NITROSOMONAS (STATIONS 252 AND 258)

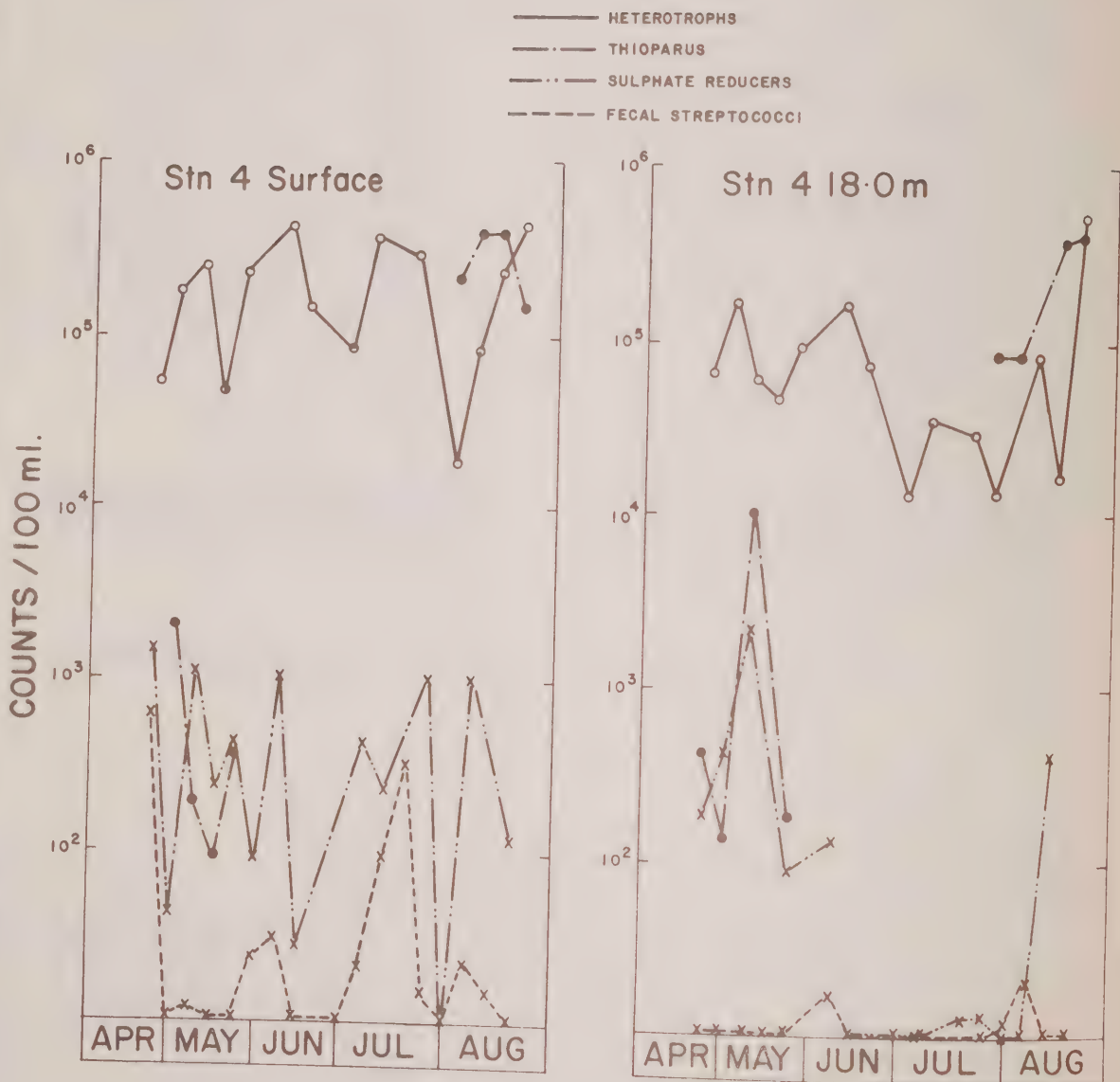


FIGURE 3a: TEMPORAL DISTRIBUTION OF HETEROTROPHS, SULFUR OXIDIZERS AND REDUCERS AND FECAL STREPTOCOCCI (STATION 4)

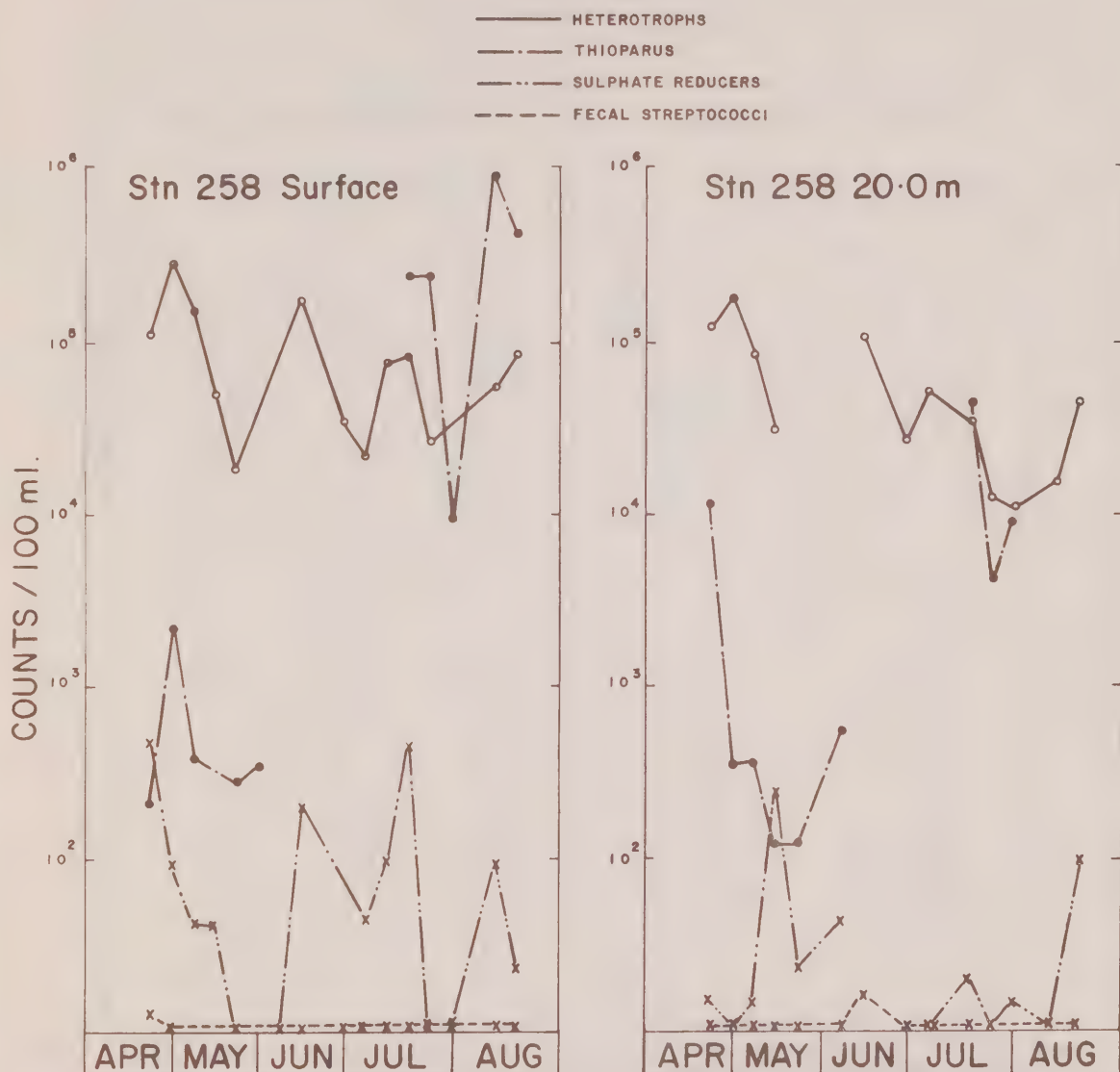


FIGURE 3b. TEMPORAL DISTRIBUTION OF HETEROTROPHS, SULFUR OXIDIZERS AND REDUCERS AND FECAL STREPTOCOCCI (STATION 258)

— HETEROTROPHS
 - - - THIOPARUS
 — · — · — SULPHATE REDUCERS
 - - - - - FECAL STREPTOCOCCI

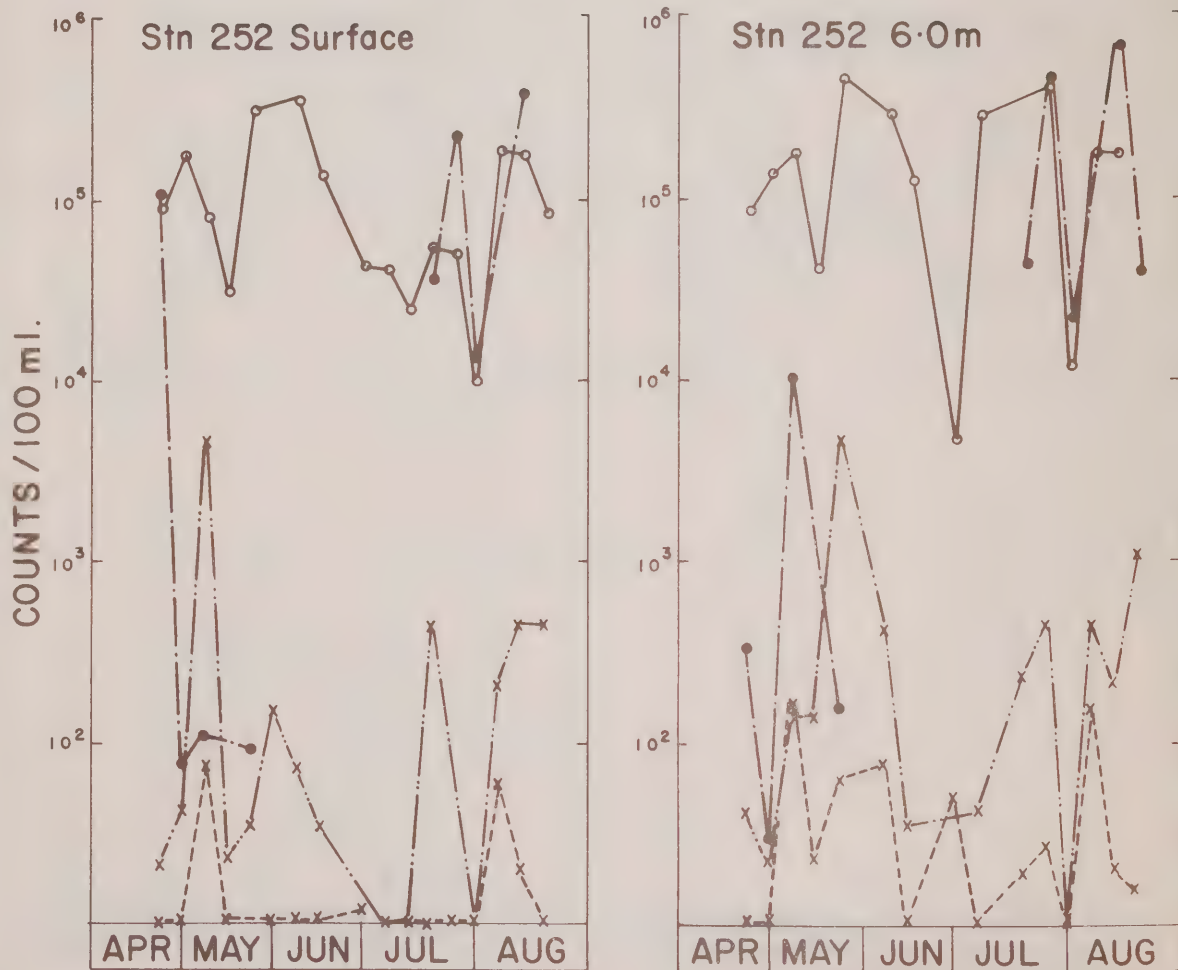


FIGURE 3c : TEMPORAL DISTRIBUTION OF HETEROTROPHS,
 SULFUR OXIDIZERS AND REDUCERS AND FECAL STREPTOCOCCI
 (STATION 252)

— HETEROTROPHS
 - - - THIOPARUS
 - · - · - SULPHATE REDUCERS
 - - - FECAL STREPTOCOCCI

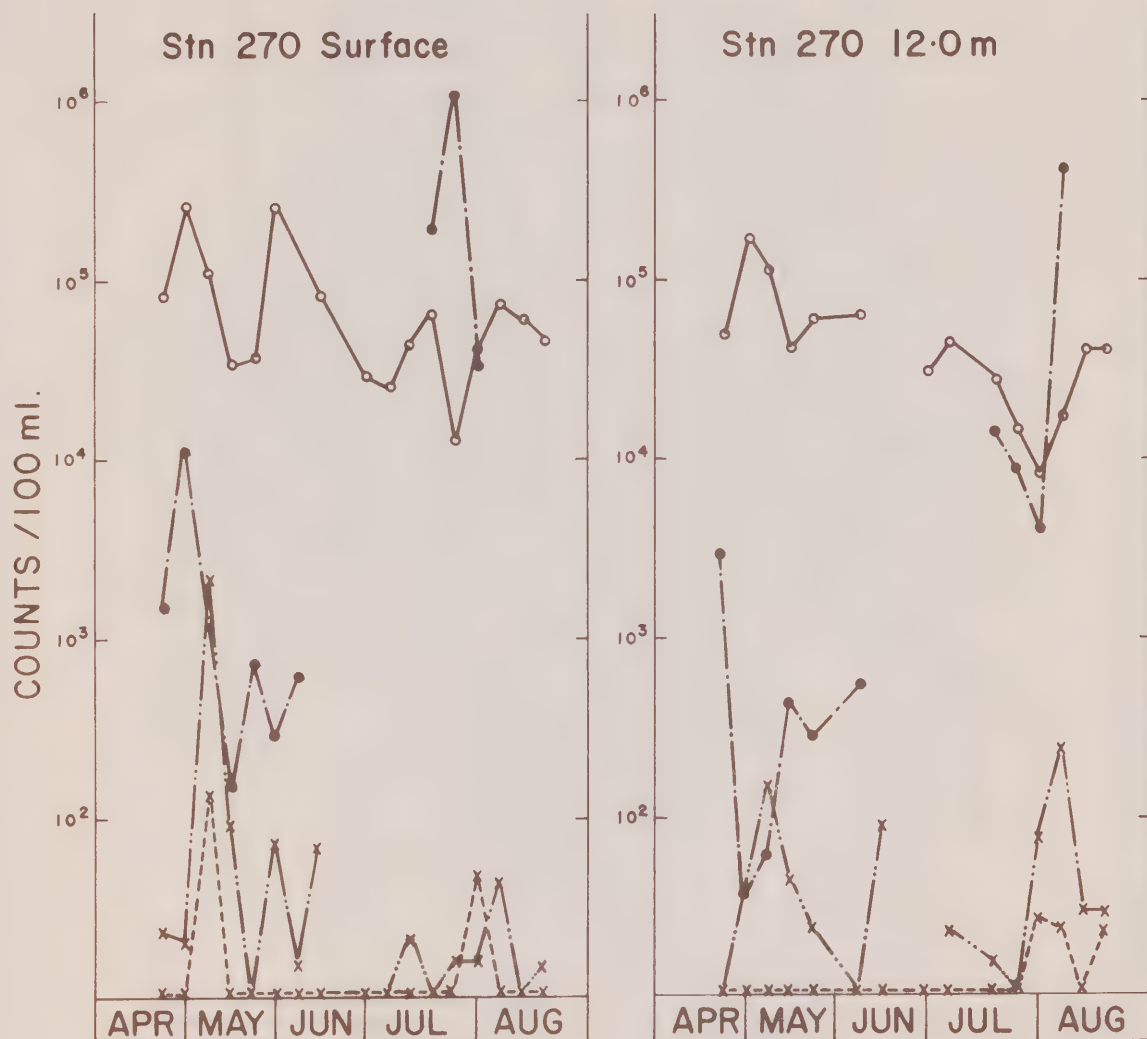


FIGURE 3d: TEMPORAL DISTRIBUTION OF HETEROTROPHS,
 SULFUR OXIDIZERS AND REDUCERS AND FECAL STREPTOCOCCI
 (STATION 270)

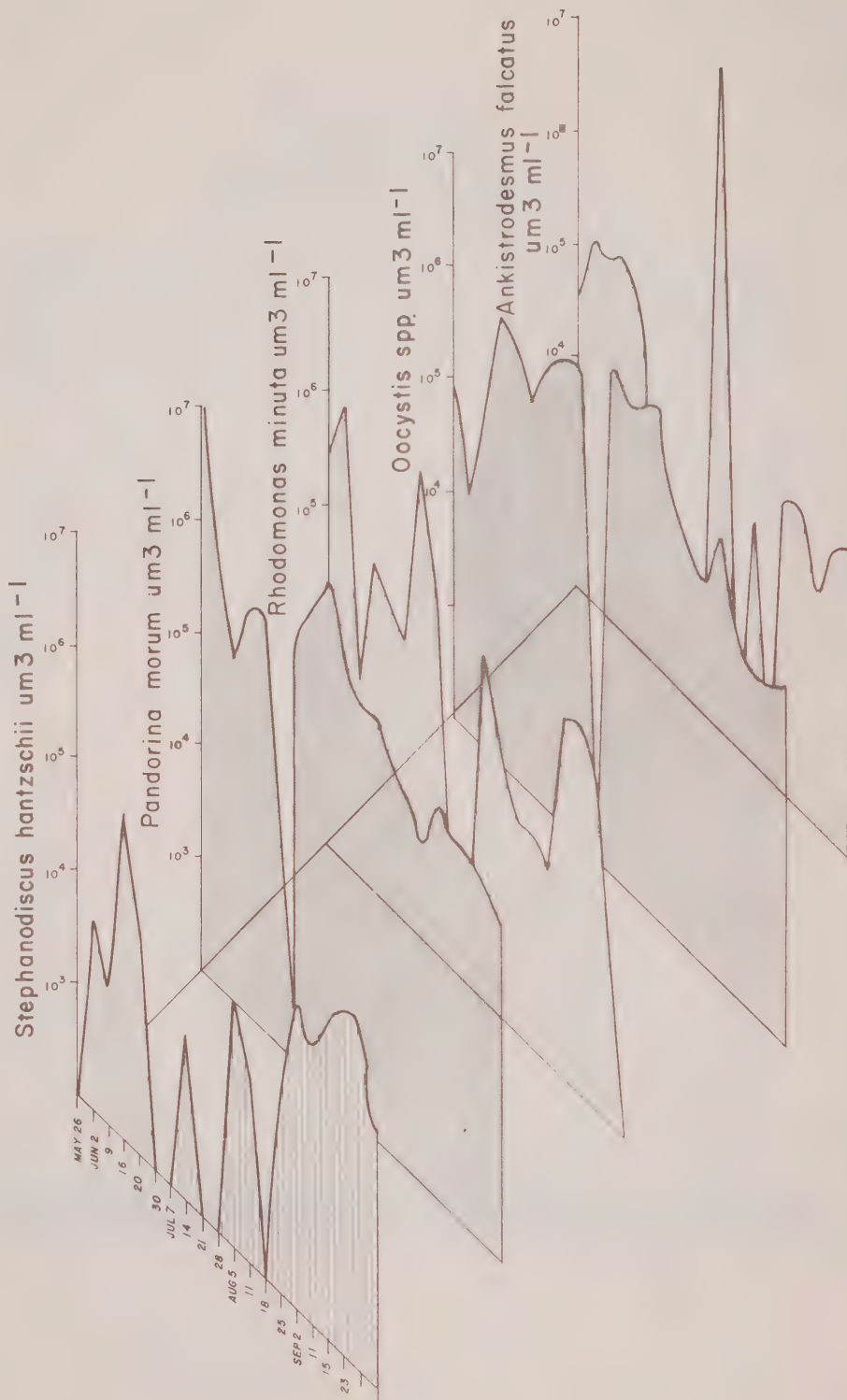


FIGURE 4a : TEMPORAL DISTRIBUTION OF THE COMMON PHYTOPLANKTON AT STATION 258

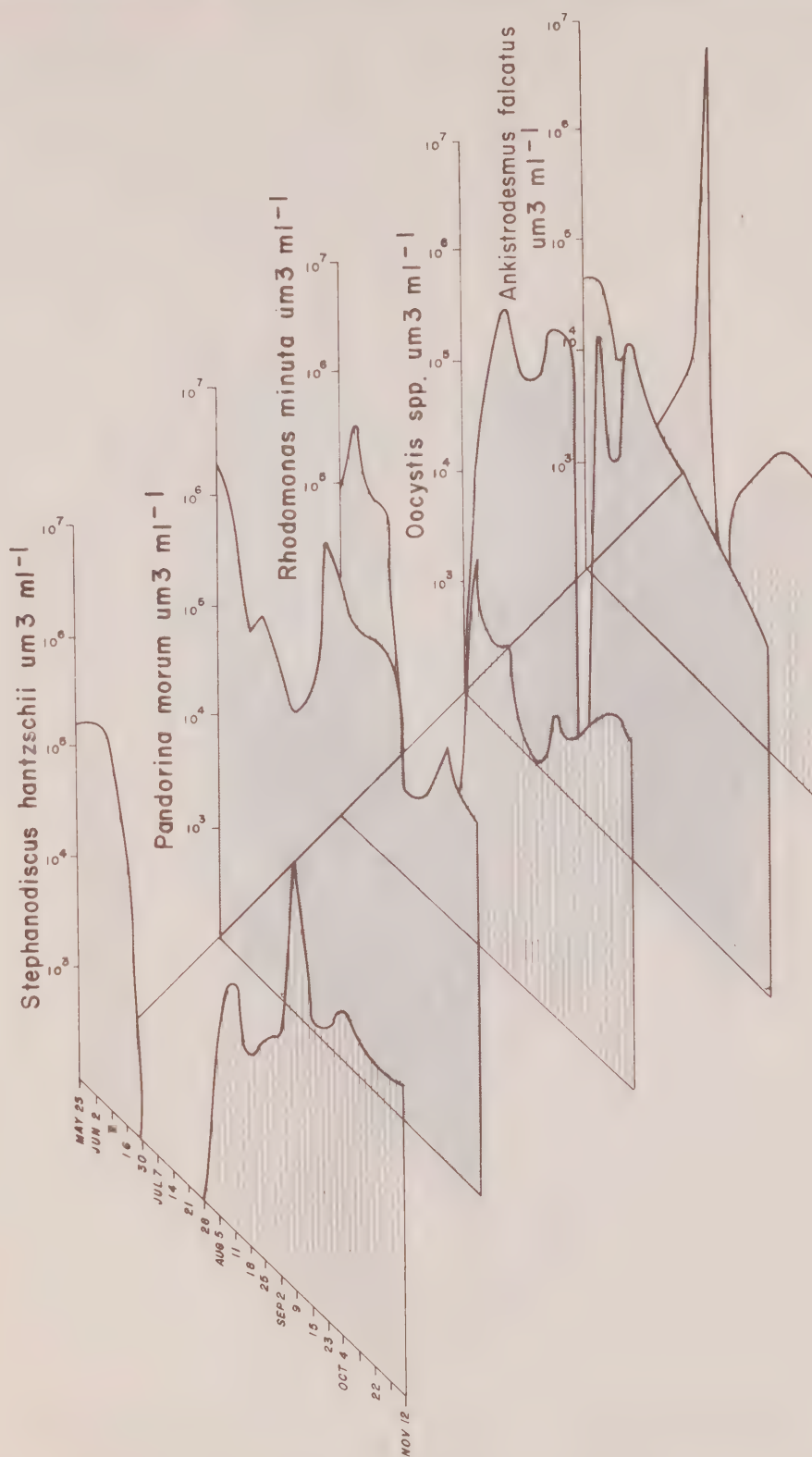


FIGURE 4b: TEMPORAL DISTRIBUTION OF THE COMMON PHYTOPLANKTON AT STATION 4

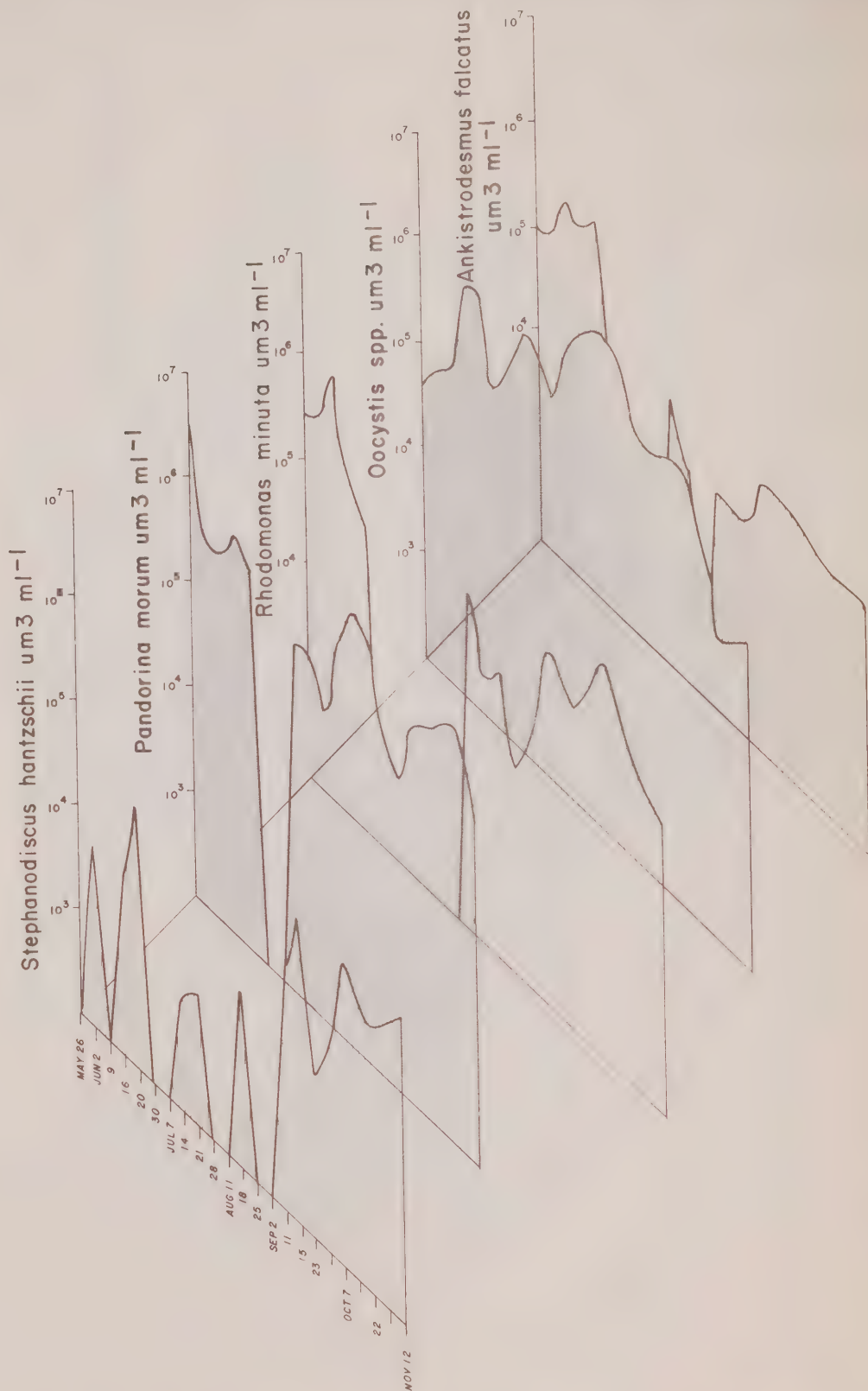


FIGURE 4c : TEMPORAL DISTRIBUTION OF THE COMMON PHYTOPLANKTON AT STATION 252

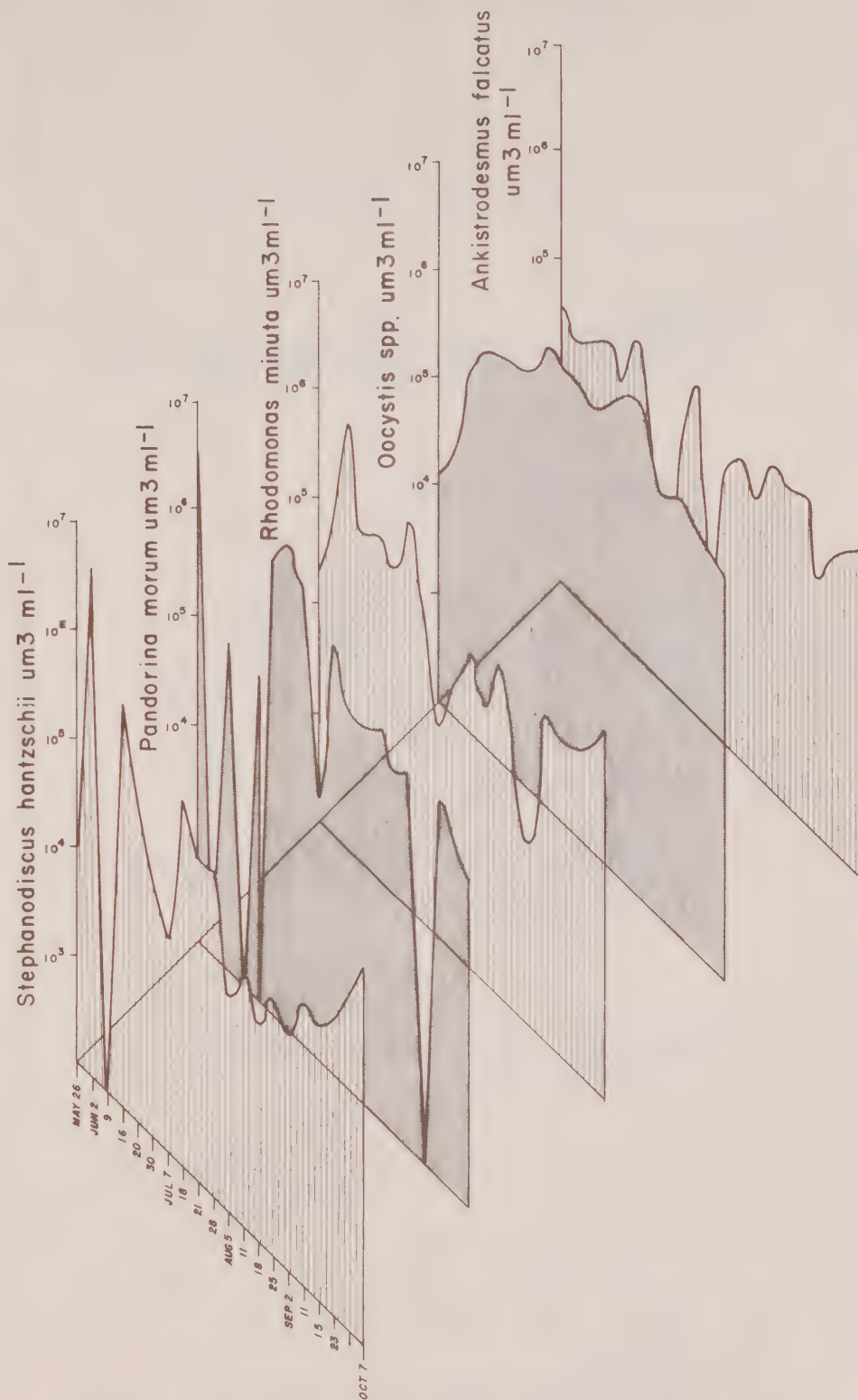


FIGURE 4d : TEMPORAL DISTRIBUTION OF THE COMMON PHYTOPLANKTON AT STATION 270

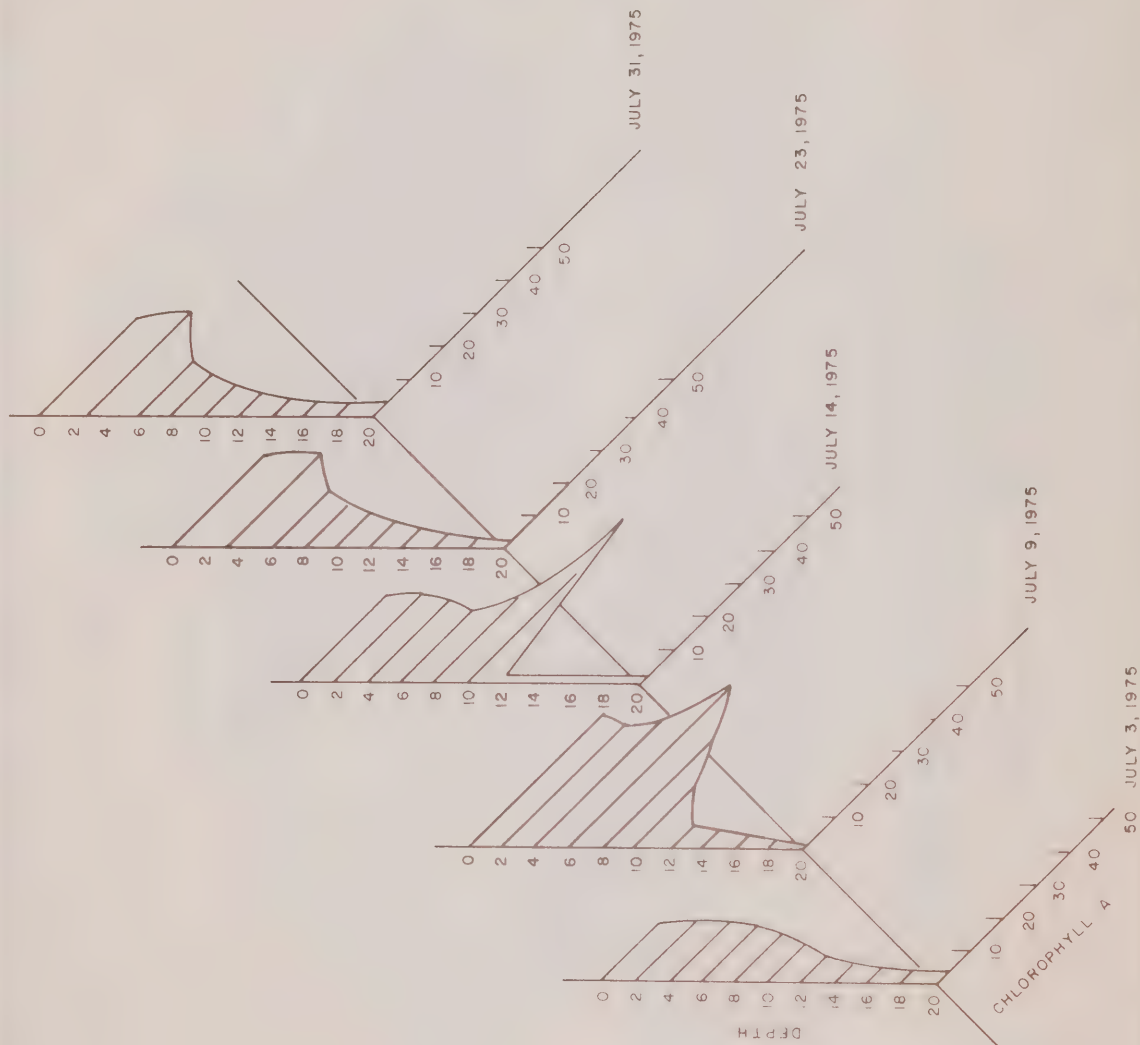


FIG. 5 : CHLOROPHYLL *a* DISTRIBUTION DURING THE MIXING PERIOD AT STATION 258, 1975.

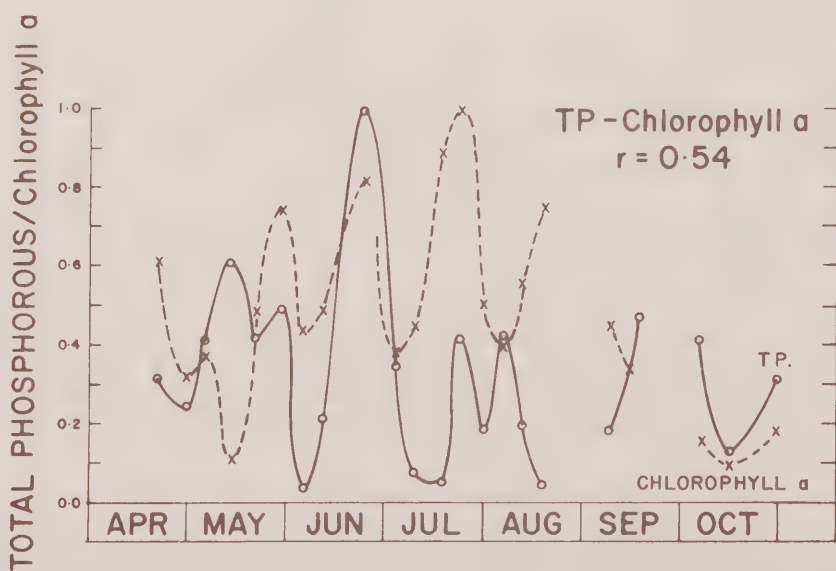
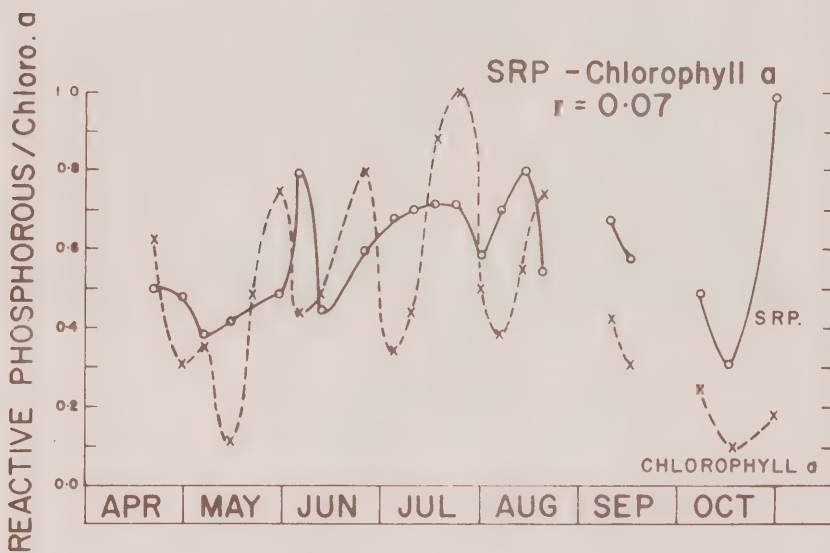
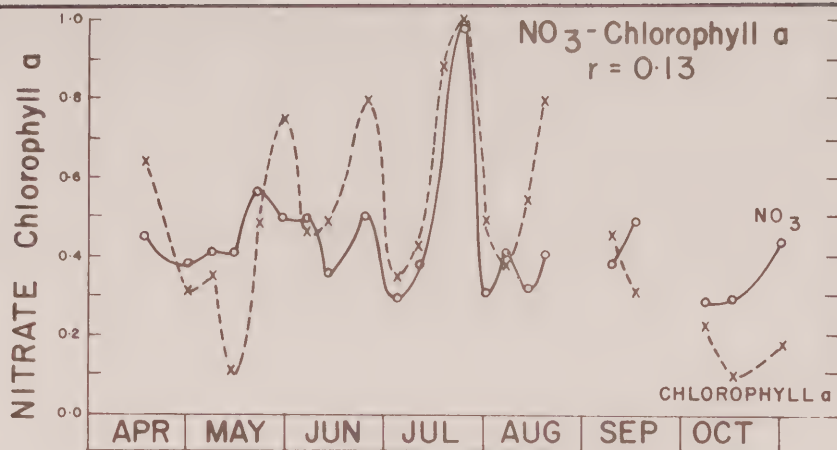


FIGURE 6: RELATIVE VARIATIONS OF NITRATE AND PHOSPHORUS AS RELATED TO CHLOROPHYLL a

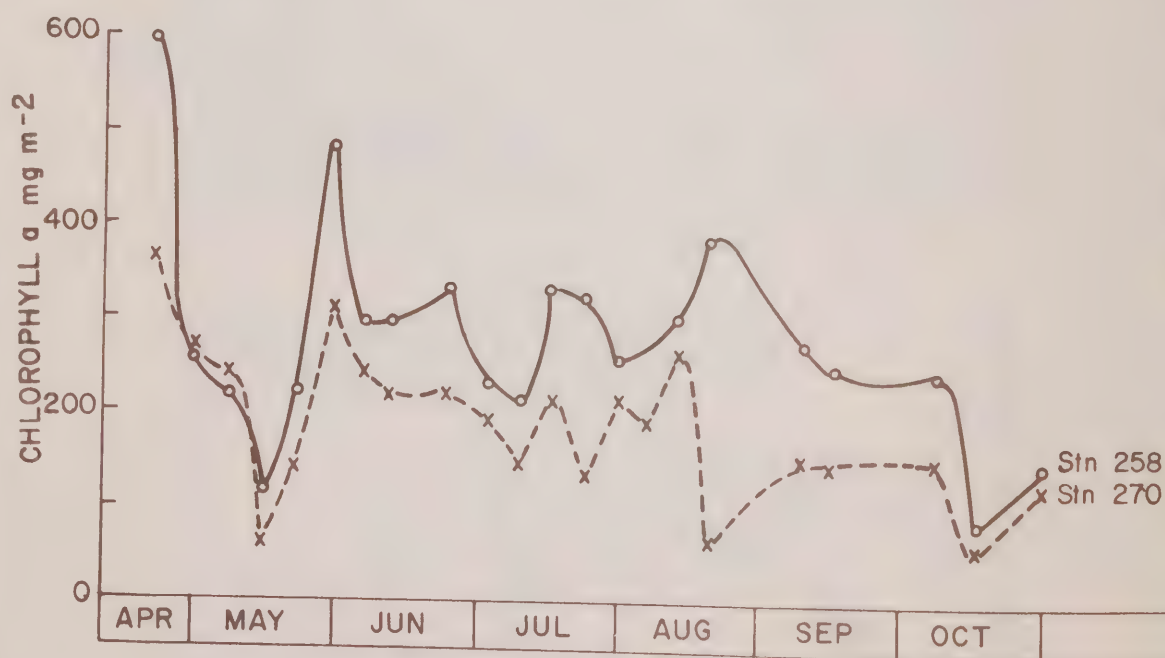


FIGURE 7 : PHYTOPLANKTON STANDING CROPS AT STATIONS 4, 252, 258 AND 270 (Chlorophyll *a* mg m⁻²)

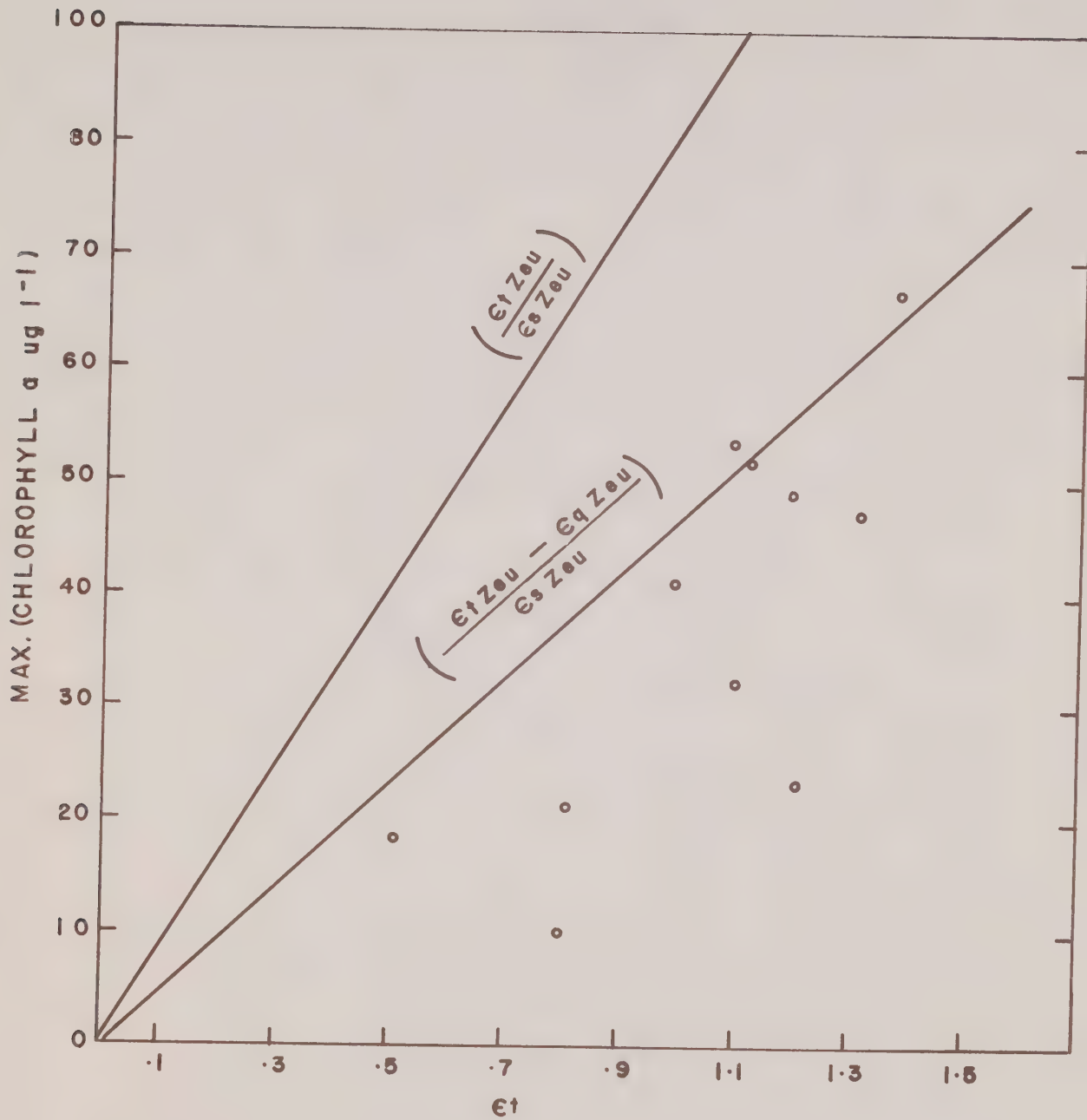


FIGURE 8 : THEORETICAL STANDING CROPS AS RELATED TO BACKGROUND ATTENUATION

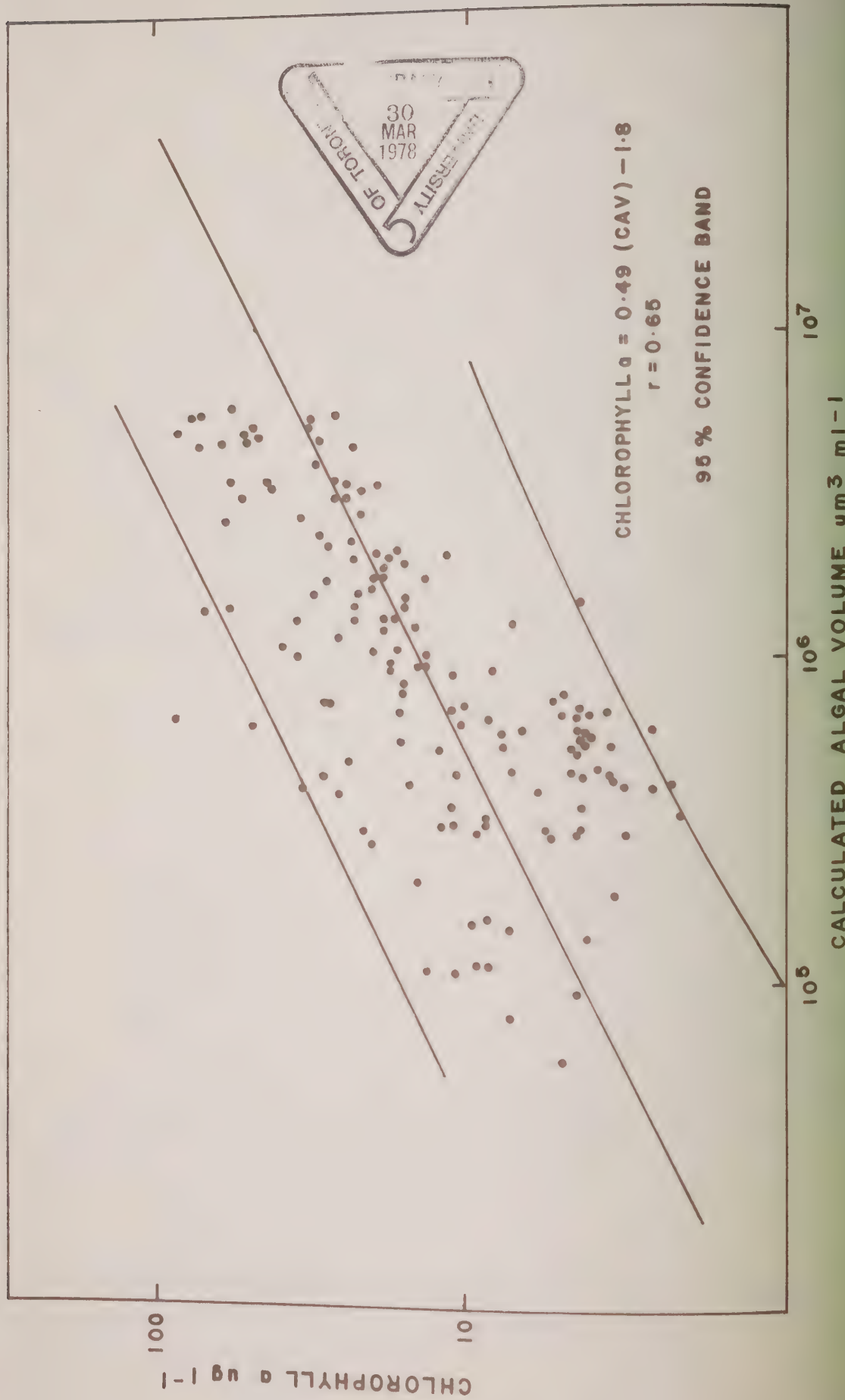


FIGURE 9: RELATION OF CHLOROPHYLL a ($\mu\text{g/l}$) AND CALCULATED ALGAL VOLUME ($\mu\text{m}^3/\text{ml}$)



